



Current state of knowledge when it comes to consumer exposure to nanomaterial embedded in a solid matrix

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Published in:
Sustainable Nanotechnology Conference 2015

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Mackevica, A., & Hansen, S. F. (2015). Current state of knowledge when it comes to consumer exposure to nanomaterial embedded in a solid matrix. In *Sustainable Nanotechnology Conference 2015: Conference abstracts*

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Sustainable Nanotechnology Conference 2015

A Joint EU - US Conference

VENICE, ITALY

9 - 11 March 2015

CONFERENCE ABSTRACTS 2015



ORGANIZERS



Plenary Lecture 1

Nanotechnology Path to Sustainable Society

Mihail Roco (National Science Foundation and National Nanotechnology Initiative)

Abstract: Nanoscale science and engineering supports a foundational technology with implications on sustainability of economy, environment and overall societal development. Special challenges are balanced, equitable and safe affirmation of the technology. By establishing controlled synthesis and processing of matter at the nanoscale, nanotechnology would require fewer amounts of materials, water, and energy; and with the high degree of precision in nanomanufacturing we are generating less pollution for the same functionality. This presentation will focus on evolution of priorities since 2000. The long-view of nanotechnology development has three stages, each dominated by a different focus: phenomenological basics and synthesis of nanocomponents (2000-2010), nanosystem integration by design for fundamentally new products (2010-2020), and creation of new technology platforms based on new nanosystem architectures (2020-2030)(www.wtec.org/nano2/). Such development raises significant sustainability opportunities and challenges. Nanoscale science and engineering is expected to converge with biotechnology, information technology, cognitive technologies and other knowledge and technology domains resulting in an increase of the complexity and uncertainty of the secondary effects (*"Converging Knowledge, Technology and Society: Beyond Nano-Bio-Info-Cognitive Technologies"*, Springer 2013, www.wtec.org/NBIC2-Report/). Nanotechnology development and sustainability are seen as two key interdependent invariants for future society. Convergence principles can provide guidance how to plan and better implement sustainable nanotechnology.

Session 1A Occupational & Consumer Exposure

Current state of knowledge when it comes to consumer exposure to nanomaterial embedded in a solid matrix

*Aiga Mackevica (DTU Environment, Technical University of Denmark)**

Steffen Foss Hansen (DTU Environment, Technical University of Denmark)

Abstract: Little is known about consumer exposure to engineered nanomaterials (ENMs) stemming from NM-containing consumer products. Here, we focus especially on studies that have investigated the release of ENMs from consumer products, investigating to what extent the information in the open literature can be used to fulfill the requirements outlined in the European chemical legislation, REACH. In total, we have identified about 75 publications of relevance and the number of publications is increasing every year. The most studied materials include silver and titanium dioxide NPs, CNTs and SiO₂. If reported, we summarized the studies by identifying nanomaterial(s), product name, product type, Product or Article Category according to REACH; experimental setup, total content in product, information on release, techniques used for characterization of nanomaterials both in product matrix and in the released form. For studies that report enough information, we developed potential exposure scenarios and derived exposure estimates according to REACH R.16 using the Tier 1 equations for consumer exposure estimation and Tier 1 tools i.e. ECETOX TRA and Consexpo. In general, we find that the information and data provided by each of the studies rarely contain all the information entries that one would need to complete exposure assessments according to REACH.

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Session 1A Occupational & Consumer Exposure

Can Weathering and Processing Release a Nanoscale Transparent Organic Pigment from the Polymer Matrix of Consume Products?

*Nicole Neubauer (BASF SE)**

Wendel Wohlleben (BASF SE)

Abstract: As nanomaterial containing materials may undergo changes during their production, use, and disposal, it is highly desirable to include their whole life cycle into an assessment of their safety. Coloristic pigments are used ubiquitously to give colour to plastics and paints. However, there is a knowledge gap with regard to their nano-specific safety. Therefore, we studied the release of an organic pigment (Red 254) from a PE matrix after weathering or processing by drilling and sanding. Representative for a final product (e.g. car bumper) small plates were investigated. After weathering according to ISO protocol 4892-2, release measurements were performed by centrifugation, spectroscopy and gloss retention. The results clearly demonstrated that the amount of release particles is below the limit of quantification of 10 ppm. In addition, no changes of the plate surface as wells as no free nanoparticles could be observed which was investigated by electron microscopy and XPS (X-ray photoelectron spectroscopy). Drilling and sanding of the plates were realized in an aerosol chamber. Number, size and morphology of the released fragments were determined by well-established aerosol measurement techniques and by electron microscopy, and show correlation with shear forces.

Session 1A Occupational & Consumer Exposure

Exposures to Nanoparticles and Fibers during Manufacturing and Recycling of Polycarbonate Carbon Nanotube composites

*Dhimiter Bello (UMass Lowell, Dept. Work Environment)**

Pongsit Boonruksa (UMass Lowell, Dept. Work Environment)

Jlnde Zhang (UMass Lowell, Dept. Plastics Engineering)

Jacqueline Isaacs (Northeastern University, Dept. Mechanical & Industrial Engineering)

Susan Woskie (UMass Lowell, Dept. Work Environment)

Joey Mead (UMass Lowell, Dept. Plastics Engineering)

Abstract: This study investigated airborne nanoparticle exposures generated during injection molding and grinding of polycarbonate carbon nanotube composites (PC/CNT). Particle number concentration and size distribution were measured using a suite of real time instruments. Area samples were collected using an electrostatic precipitator and examined by transmission electron microscopy for particle morphology. Breathing zone samples were collected on nucleopore filters. Respirable fibers were counted with a scanning electron microscope. The results showed that processing and grinding during recycling of PC/CNT released airborne nanoparticles with a geometric mean (GM) particle concentration from 4.71×10^3 to 1.75×10^6 particles/cm³. The ratios of GM particle concentration measured during the process to the background particle count were high up to 1.3 (loading), 1.9 (melting), and 1.4 (molding), and 101 (grinding), indicating significant nanoparticle emissions from these processes. The various particle morphologies were observed including respirable and nanoscale particles, particles with protruding CNTs, and fibers, but no free CNTs. The breathing zone respirable fiber concentration during grinding ranged from non-detectable to 0.13 fiber/cm³. No clear evidence that nanoparticle exposures were affected by the number of recycling cycles (up to 20). Exposures controls should be instituted during synthesis, processing and recycling of PC/CNT composites.

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Session 1A Occupational & Consumer Exposure

Evaluation of Nano Exposure Models

*Wouter Fransman (TNO)**

Eef Voogd (TNO)

Derk Brouwer (TNO)

Abstract: A previously developed conceptual model (Schneider et al., 2011) offers a framework to describe the processes that affect the emission (at the source) and the fate of manufactured nanoparticles during transport to the receptor. This model was used to critically review available models for estimating occupational and consumer exposure and their applicability for exposure to NOAA. A selection of these models (ART and Stoffenmanager Nano) was additionally evaluated by using existing exposure data to test the relative performance. Measurement data from various exposure scenarios with Al₂O₃, SiO₂, and TiO₂ measured with the SMPS and APS were selected based on data availability and data quality. Correlation between model estimations and (metric converted) measured concentrations were calculated using both Spearman and Pearson correlation. For two of the three substances tested in this performance check, the ART estimations fit good. Also the Stoffenmanager Nano showed a trend matching the measurement data for the same substances. It is strongly advised to expand this performance check to more activities and thus more variation in exposure concentrations, but also to other exposure estimation tools.

Session 1A Occupational & Consumer Exposure

Inhalation exposure and dermal deposition of airborne particles during electrostatic spraying of liquid TiO₂-based nanocoating

*Antti J. Koivisto (National Research Centre for the Working Environment)**

Ismo K. Koponen (National Research Centre for the Working Environment)

Alexander C.Ø. Jensen (National Research Centre for the Working Environment)

Kirsten I Kling (National Research Centre for the Working Environment)

Marcus Levin (National Research Centre for the Working Environment)

Asger W. Nørgaard (National Research Centre for the Working Environment)

Keld A. Jensen (National Research Centre for the Working Environment)

Abstract: Exposure assessment models are increasingly being used for regulatory purposes. Risk assessments should cover all potential exposure routes where inhalation, ingestion and dermal are most common pathways for uptake. Here, we measured particles dispersion and deposition during electrostatic spraying of liquid coating product containing TiO₂ nanoparticles in a 20 m³ chamber. The ventilation rate was 0.5 h⁻¹ while the temperature and relative humidity was 23 °C and 50 %, respectively, corresponding to typical indoor environment atmospheric conditions. Surfaces of tiles and wallpaper (2 m²) were sprayed for 15 and 150 seconds to mimic low and high exposure, respectively. A near field, far field, and breathing zone size-resolved concentrations were measured with a time resolution of 1 second. For electron microscopy analysis, we collected samples of deposited particles from walls, floor, and worker knee, hand, and face. This will show relative particle deposition on the worker when compared to the chamber surfaces. Preliminary results show that the air was fully mixed inside the chamber after few seconds from the start of spraying. Thus, here the particles dispersion can be described with a single zone model. This study will be used in parameterization of the inhalation and dermal exposure assessment model.

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Session 1A Occupational & Consumer Exposure

The Key Role of Workplace Exposure Assessment in Creating a Legacy of Sustainability

Chuck Geraci (National Institute for Occupational Safety and Health)

Abstract: The volume of Engineered Nanoscale Materials (ENM) being used globally for commercial applications is increasing every year. At the same time, the scientific community continues to investigate potential human health hazards from exposure to certain types of ENMs. In order to realize the full potential of this versatile class of materials, it is important to understand the relative risks and how to manage them properly and effectively along their life cycle. Meaningful characterization of potential health risk requires a good understanding of actual exposures. The first opportunity for human exposure to any new material, including ENMs, is in the workplace, which is why there is a need to understand occupational exposures more completely. At present, knowledge of actual worker exposure and resulting risk has been limited but is increasing. Accurate exposure assessment is a key element in the overall process of characterizing risk, developing good practices, and assisting in prioritizing work on occupational exposure limits (OEL) for ENMs. As a nanomaterial moves through its life cycle; as a pure material, as an intermediate, and as a component in a final product, it is important to understand the potential for exposure at the different stages. Exposure data can shape the practices, and even material or product designs, that contribute to safe and responsible deployment of the technology. In reality, the workplace represents the first opportunity to develop a legacy of success for EHS and sustainability for a nanomaterial-enabled product. A variety of approaches are being used to evaluate worker exposure and movement toward consistency and harmonization of measurement techniques is evolving. Central to all the approaches used is the task of quantifying actual exposure in support of a risk-focused strategy and the development of a responsible approach to developing commercial and consumer applications of ENMs. Until more is known, a prudent, risk-based approach to management of ENMs in the workplace is needed. This presentation will summarize some of the key research being conducted in the area of occupational exposure assessment for nanomaterials.

Session 1B Ecotoxicology, effects on ecosystem services & ecological risks

Fish cell lines as in vitro models for ecotoxicology testing of engineered nanomaterials

*Azucena Bermejo-Nogales (INIA)**

Maria Luisa Fernandez-Cruz (INIA)

José María Navas (INIA)

Abstract: Fish cells maintained in vitro constitute an interesting tool to obtain information about the toxic action of a wide variety of substances, including nanomaterials, facilitating their prioritization for further testing or even being used directly in risk assessment. The aim of the present study was to assess the toxicity of a broad array of ENM (CeO₂, multiwall carbon nanotubes (MWCNT), SiO₂, silver, TiO₂ and ZnO obtained from the JRC repository) using two fish cell lines as in vitro models: the topminnow fish (*Poeciliopsis lucida*) hepatoma cell line (PLHC-1) and the rainbow trout (*Oncorhynchus mykiss*) fibroblast-like gonadal cell line (RTG-2). Cytotoxicity was evaluated after 24 h of exposure with alamarBlue, CFDA-AM and neutral red assays. Exposure to ENM resulted in a cell- and dose-dependent increase of cytotoxicity being PLHC-1 the most sensitive cell type. The ENMs used exhibited the following ranking in toxicity: Ag>ZnO>MWCNT = SiO₂=TiO₂=CeO₂. Alterations of lysosome functionality and disruption of metabolic activity were the primary mechanisms of toxic action of AgNM and ZnONM, respectively. This study shows the appropriateness of fish in vitro models to shed light on the mechanisms underlying the toxic action of ENM, information that can be used in the framework of intelligent testing strategies. Acknowledgements: this work was financially supported by FP7 MARINA project (263215).

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Session 1B Ecotoxicology, effects on ecosystem services & ecological risks

Mechanisms underlying the enhancement of toxicity caused by coincubation of ZnO and Cu nanoparticles

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David Hernandez-Moreno (INIA)

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Connolly M. (INIA)

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Abstract: The purpose of the study was to determine the mechanisms underlying the enhancement of toxicity produced by co-incubation of copper (CuNPs) and zinc oxide nanoparticles (ZnONPs) in the fish hepatoma cell line PLHC-1 after 48 h of exposure. Cells were exposed to CuNP 50 nm at a range of concentrations (0.39 - 25.0 $\mu\text{g/mL}$), alone or in combination with ZnONP (25 and 100 nm) at a non-toxic concentration of 6.25 $\mu\text{g/mL}$. For both NPs, cells were exposed to suspensions (nanoparticles) or to supernatants (ions), and their combinations. Viability of cells was evaluated by the MTT cytotoxicity assay. Data about the characterization and behavior of the NPs in the cells was obtained by TEM, DLS and ICP-MS. Cytotoxicity was enhanced when cells were coexposed to both NPs suspensions and after exposure to CuNPs supernatant and ZnONPs 25 nm suspension. Metal content was evaluated for each combination of CuNPs and ZnONPs suspensions and supernatants. The intracellular concentration of Cu remained stable whereas Zn increased significantly when cells were exposed to: 1) ZnONP supernatants and CuNPs suspensions, 2) ZnONP suspensions and CuNP supernatants. Further studies by TEM are conducted to elucidate this mechanism. Acknowledgements: INIA project AT2011-001 and FP7 project GUIDEnano 604387.

Session 1B Ecotoxicology, effects on ecosystem services & ecological risks

Copper nanoparticles or compounds impact agronomic and physiological parameters in cilantro (*Coriandrum sativum*)

*Nubia Zuverza-Mena (UTEP)**

Illya A. Medina Velo (UTEP)

Jorge L. Gardea-Torresdey (UTEP)

Abstract: In this study, copper-based nanoparticle (NP) or compounds are investigated for their potential harm to the environment, using cilantro as the model species. Cilantro plants were exposed to $\text{Cu}(\text{OH})_2$, nanosized copper (nCu), micro-sized copper (uCu), nanosized copper oxide (nCuO), micro-sized copper oxide (uCuO), and CuCl_2 at 20 and 80 mg/kg soil. After 30 days exposure, plant size, Cu accumulation, and chlorophyll content were measured by a ruler, inductively coupled plasma-optical emission spectroscopy (ICP-OES), and SPAD chlorophyll meter, respectively. Results showed no effects on root length, but shoot elongation decreased by 12.4% on plants exposed to 80 mg/kg nCu and by 11 % in plants exposed to uCuO at 20 and 80 mg/kg. ICP-OES results showed a reduction trend in root copper of all treatments, even though no statistically significant differences were evident compared to control; while the amount of copper in shoots was significantly higher for all treatments, compared to control. Chlorophyll content decreased significantly on plants exposed to 20 mg/kg uCuO, but increased on plants exposed to $\text{Cu}(\text{OH})_2$, nCu, and uCuO at 80 mg/kg. Overall, uCuO showed higher toxicity to cilantro, compared to nanoparticulate copper.

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Session 1B Ecotoxicology, effects on ecosystem services & ecological risks

Trophic Transfer Potential of Nanoparticles In Terrestrial Food Chains

*Jason White (CT Agricultural Experiment Station)**

Roberto De la Torre-Roche (CT Agricultural Experiment Station)

Joseph Hawthorne (CT Agricultural Experiment Station)

Abstract: Bulk or nanoparticle (NP) cerium and lanthanum oxide were added to soil (0, 500, 1000 mg/kg) with zucchini or lettuce. After 28 days, the plant Ce and La content was determined and leaves were fed to crickets or darkling beetles for 14 days. The herbivores were fed to wolf spiders or mantids for 7 days. The Ce and La content of arthropods and feces was measured. NP exposure had little effect on total mass, although nanoceria suppressed zucchini flower production. Zucchini Ce content was greater with the NP exposure. The flowers, leaves, stems, and roots of bulk plants contained 93.3, 707, 331, and 119,000 ng/g, respectively; NP-exposed plants contained 153, 1510, 479 and 567,000 ng/g, respectively. Crickets fed bulk and NP-exposed leaves contained 15 and 34 ng/g, respectively. Spiders consuming bulk-exposed crickets had non-detectable Ce but NP-fed spiders contained Ce at 4.9 ng/g. For La, there was no difference in lettuce content based on particle size. Although NP-exposed crickets contained less La than the bulk, mantid La content did not differ with particle size. These findings show that some nanoparticles may bioaccumulate at levels greater than bulk materials and that this can result in trophic transfer and food chain contamination.

Session 1B Ecotoxicology, effects on ecosystem services & ecological risks

The effects of nanomaterials on individual species and ecosystem services

*Teresa Fernandes (Heriot-Watt University, UK)**

Simon Little (Heriot-Watt University, UK)^p

Helinor Johnston (Heriot-Watt University, UK)

Abstract: The use of nanomaterials is widespread in a range of applications and products and it is therefore expected that they will eventually end up in the environment, although it is unclear what form that may take. The environmental effects of nanomaterials are now widely investigated on a range of organisms and endpoints. Nevertheless there is still lack of information on their effects on benthic systems, which are considered to be sinks of chemicals in the natural environment, particularly in the long term. In addition, studies on the impacts of nanomaterials on ecosystem services are virtually non-existent.

As the main recipient of industrial and domestic wastewaters, the fate and behaviour of nanomaterials in aquatic systems has come under much scrutiny in recent years. Due to the processes of aggregation, agglomeration and sedimentation, sediment habitats in particular are anticipated to be the final sink for nanomaterials, however, little is still known in terms of the effects on sediment fauna. This research, funded by the FP7 MARINA project, aims to investigate the toxicity of two reference engineered nanoparticles, OECD silver (NM-300K) and titanium dioxide (NM-104) towards the freshwater, sediment ingesting oligochaete, *Lumbriculus variegatus*. Toxicity tests incorporating *L. variegatus* survival, reproduction and biomass were carried out in formulated sediment (28 days) whilst reconstituted OECD medium was used to assess short-term, (96 hour) aquatic toxicity. Alterations to abiotic conditions (natural organic matter content, ionic strength and pH) proved to influence toxicity in both medium and sediment exposures. Sub-lethal effects upon behaviour were explored as a sensitive, non-destructive, biomarker, whilst antioxidant enzyme activity (superoxide dismutase and catalase) and lipid peroxidation were used to investigate the mode through which nanoparticles exerted toxicity.

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Session 1C Life Cycle Thinking & LCA

Contribution of nanotechnology and nanomaterials to increased sustainability of industrial products and processes

*David G. Rickerby (European Commission Joint Research Centre)**

Andreas N. Skouloudis (European Commission Joint Research Centre)

Abstract: An overview is presented of some of the opportunities for nanotechnology in real-world industrial applications. A wide range of industries and manufacturing processes are already being or are likely to be impacted by current advances in nanotechnology and nanomaterials. Significant improvements in energy and resource efficiency could potentially be achieved by the implementation of nanotechnology in industrial settings. Developments in nanomaterials can be expected to reduce energy and raw materials consumption and emissions through cleaner, less wasteful production methods. This should ultimately assist in the creation of greener manufacturing processes and a low carbon economy. Examples are given illustrating the advantages of nanomaterials in diverse industrial sectors such as electronics, aerospace, construction, energy, water, catalysts and forest products. The essential role of life-cycle analysis in evaluating the sustainability of nanotechnology enabled products and risk assessment for identifying the health and environmental effects of nanomaterials is discussed.

Session 1C Life Cycle Thinking & LCA

Brazilian scenario in sustainable nanotechnology

*Rachel Horta Arduin (IPT)**

Natalia Neto Pereira Cerize (IPT)

Claudia Echevengua Teixeira (IPT / Uninove)

Abstract: Nanoscale materials are used in diverse areas, and the huge potential of these technologies resulted in a considerable growth in investment in research and development worldwide. Since the 2000 the Brazilian government has set a national program to develop and disseminate nanotechnology. Brazil was the 25th country in the world ranking of publications in this field in 2006. The purpose of this work is to evaluate the scientific production related to sustainable nanotechnology in Brazil, through conducting a systematic literature review until December 2014. The criteria involved the establishment of keywords and search platforms. The articles were classified into sustainable nanotechnology (13) and life cycle assessment (2). Literature highlights that after 2010 the discussion regarding the environmental impacts of the nanotechnology has increased. The environmental aspect was usually discussed in the field of risk assessment, but few studies aimed to quantify the impacts. Two studies of life cycle assessment were identified, both cradle to gate and focused in the inventory of the production of the nanomaterial in Brazil. This paper sets out to stress that as discussed worldwide, also in Brazil the internationally standardized method of LCA can help identify opportunities for reducing environmental impacts in the entire life cycle of nanoproducts.

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Session 1C Life Cycle Thinking & LCA

New framework accounting for a spatial differentiation in the calculation of characterisation factors for the toxicity potential of nanomaterials

*Beatrice Salieri (Empa, Swiss Federal Laboratories for Materials Science and Technology)**

Martina Pini (University of Modena and Reggio Emilia)

*Roland Hirschler (Empa, Swiss Federal Laboratories for Materials Science and Technology)**

Abstract: A new modeling framework in life cycle impact assessment (LCIA) is proposed for the calculation of Characterisation Factor (CF) for nanomaterials (such as nano-TiO₂ or CNT) for toxicity impact categories. In the recently developed consensus model for ecotoxicity and human toxicity, the USEtoxTM model, the CF is calculated as the product of three factors: Fate Factor, Effect Factor, and Exposure Factor. As shown e.g. in Fantke et al., 2014, or in Sala et al., 2011, toxic impact categories need to have spatially-differentiated models due to the evidence that differences in fate, exposure and effect mechanisms can vary significantly depending on different geographical contexts. Regarding nanomaterials, their fate and exposure is actually strongly affected by the physicochemical environmental condition; for example, the water chemistry affects the main processes of aggregation and sedimentation for nanomaterials in freshwater, i.e. the fate factor. Our study here describes a spatially-differentiated fate and exposure model for the calculation of CF for the impact categories freshwater ecotoxicity and human toxicity. The project represents another step in the ongoing efforts in order to improve methods for the assessment of the environmental sustainability of nanomaterials.

Session 1C Life Cycle Thinking & LCA

Approach for Human Toxicity and Freshwater Ecotoxicity midpoints determination for their inclusion in Life Cycle Assessment of nanotechnology-based products

*Carme Hidalgo (LEITAT Technological Center)**

David González-Gálvez (LEITAT Technological Center)

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Socorro Vázquez-Campos (LEITAT Technological Center)^P

Abstract: The increasing use of nano-enabled products has brought controversy due to the lack of data on their potential impact on human health and environment. On that concern, there is a consensus that Life Cycle Assessment (LCA) is a suitable method to assess the environmental performance of this new technology, although LCA for nanotechnologies is challenging since there are a lot of uncertainties and data gaps and it is necessary to adapt some of the methodologies to determine the impacts of released nanomaterials. The NanoPolyTox project was designed to fill in some of these data gaps for nanocomposite applications, specifically focusing on the determination of Human Toxicity (HT) and Freshwater Ecotoxicity (FE), which contribute to damage on Human Health and on Ecosystems respectively. An approach for the determination of HT and FE impact characterization factors of released nanomaterials and their application on the evaluation of the environmental impacts of three polymeric nanocomposites for outdoors applications (MWCNT-PP, TiO₂-PA, ZnO-EVA) will be presented. This approach is based on a combination of release quantification over the different life-cycle stages (including use phase simulations and end-of-life treatments), fate modeling (using USEtox[®] as a starting point) and (eco)toxicity studies.

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Session 1C Life Cycle Thinking & LCA

Precious metal recovery from nanowaste for sustainable nanotechnology: Current challenges and life cycle considerations

Peter Vikesland (Virginia Tech)

Paramjeet Pati (Virginia Tech)

Abstract: The increasing use of nanomaterials poses new challenges for their disposal and waste management. Moreover, several nanotechnologies employ resource-limited materials, such as precious metals and rare earth elements. It is therefore essential to develop strategies to recover and recycle these materials from nanowaste, and thus make nanotechnology more sustainable. However, at present, neither well-established protocols nor federal regulations exist for nanowaste management and precious metal recovery from nanowaste. To address this issue, we developed laboratory-scale methods to recover gold from nanowaste. For our initial experiments, we used potassium tetrabromaurate and citrate-coated gold nanoparticles (AuNPs) as simulated waste. Alpha-cyclodextrin was used to recover gold via selective complexation, followed by downstream treatments to form chloroauric acid. Finally, the chloroauric acid from recovered gold was used to make new AuNPs. Besides developing new methods for recovering and recycling gold from nanowaste, we are also conducting life cycle assessment to compare the scenarios of gold production with and without recycling. Our research can provide new insights into the chemistries involved in gold recovery, as well as into the life cycle considerations in nanowaste recycling. This research also has the potential to improve current waste management practices and inform future nanowaste management policies.

Session 1C Life Cycle Thinking & LCA

From laboratory to industrial scale: scale-up calculations of chemical processes for LCA

*Fabiano Piccinno (EMPA)**

Claudia Som (EMPA)

Roland Hischer (EMPA)

Stefan Seeger (University of Zurich)

Abstract: Today, several LCAs of new materials are performed based on laboratory experiments. While this is helpful in understanding the production process, it gives no indication on how the environmental impact looks like for an industrial production. This also limits the comparability with existing material that is already produced in large quantities. The scale-up of chemical processes is not such a trivial process but involves a certain understanding of the involved steps. We present a framework on how to upscale chemical production processes for LCA purposes when only laboratory experiments are available. The calculations, estimations and considerations are designed to be used by LCA practitioners with limited knowledge in the field of chemistry or chemical engineering and help to perform such a scale-up based on a logical and systematic procedure. The developed framework is illustrated on the example of a nanocellulose case study.

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Plenary Lecture 2

Benchmark nanomaterials and case studies to challenge the decision criteria of a 'multiple perspective grouping framework'

*Wendel Wohlleben (BASF SE)**

Muhammed-Adeel Irfan (BASF SE)

Nicole Neubauer (BASF SE)

Karin Wiench (BASF SE)

Robert Landsiedel (BASF SE)

Abstract: Given the vast number and diversity of materials considered as nanomaterials (NM) by the EC nanodefinition, hazard and risk assessments of each and every variant of NM are impracticable, undesirable and stand in contradiction to the legal requirement to reduce animal testing. A comprehensive multiple perspective framework combines grouping by intrinsic material properties, grouping by use, release and route of exposure, grouping by system-dependent properties ('bio-physical interactions'), grouping by uptake, biodistribution and biopersistence and grouping by early cellular and apical biological effects. Thereby, the multiple perspective framework moves away from grouping by intrinsic structure only. In the present talk, well-known benchmark NMs from the OECD sponsorship program are proposed to assign the above properties to tiers and to represent the four main groups of: passive NM, active NM, HAR NM, soluble NM. Due to the use of system-dependent properties in tier 2 (such as surface reactivity and dissolution in simulant fluids), some intrinsic properties that are often considered as essential (such as crystallinity) are not required to place a NM into the correct group. Case studies on less well-known but widespread NMs (organic pigments) challenge the tiered grouping scheme, with validation by in-vivo data.

Session 2A Toxicology and human health risks

Toxicity and biodistribution of surface chemically modified Ag nanoparticles

*Chengfang Pang (University Ca' Foscari of Venice)**

Andrea Brunelli (University Ca' Foscari of Venice)

Antonio Marcomini (University Ca' Foscari of Venice)

Danail Hristozov (University Ca' Foscari of Venice)

Abstract: With the advance in material science, silver nanoparticles (AgNPs) are modified by different surface coatings. However, how these surface modifications influence the effects of AgNPs on human health is still largely unknown. We have evaluated the toxicity and pharmacokinetics of AgNPs coated with citrate, polyethylene glycol, polyvinylpyrrolidone and branched polyethyleneimine (Citrate AgNPs, PEG AgNPs, PVP AgNPs and BPEI AgNPs, respectively). Our results demonstrated that the toxicity of AgNPs depends on the intracellular localization that was highly dependent on the surface charge. BPEI AgNPs (ζ potential = +46.5 mV) induced the highest cytotoxicity and DNA fragmentation in Hepa1c1c7. In addition, it showed the highest damage to the nucleus of liver cells which is associated with a high accumulation in liver tissues. The PEG AgNPs (ζ potential = -16.2 mV) showed the lowest toxicity, a long blood circulation, as well as a high bioaccumulation in spleen, which suggest better biocompatibility. Moreover, the adsorption ability with bovine serum albumin revealed that the PEG AgNPs has an optimal biological inertia and can effectively resist opsonization or non-specific binding to protein in mice. This toxicological data could be useful in supporting the development of safe by design AgNPs for consumer products and drug delivery applications.

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Session 2A Toxicology and human health risks

Nanotoxicology of cadmium sulfide quantum dots in different cellular models

*Nelson Marmiroli (University of Parma)**

Marta Marmiroli (University of Parma)

Roberta Ruotolo (University of Parma)

Abstract: Nanotechnology is an emerging branch of applied science and technology for designing tools and devices at the nanoscale size (1-100 nm). Engineered nanomaterials (ENMs) have been widely used in fields such as electronics, medicine, physics, chemistry, biology, but also in the food and cosmetic industries. Little is known about the molecular mechanisms of cellular uptake and biological interactions with the ENMs. Adsorption of biomolecules to nanomaterials may influence cellular uptake, inflammation, accumulation, degradation and clearance of the ENMs. Understanding such relations is crucial for generating bio-compatible nanomaterials with controlled surface characteristics in a biological environment or for ENM-targeted delivery. The aim of this work was to study the biological effects of cadmium sulfide quantum dots (CdS QDs) in different cellular models. Integrating omic approaches such as transcriptomics, proteomics and phenomics, we identify new biological pathways important for CdS QD stress tolerance in yeast (*Saccharomyces cerevisiae*), plant (*Arabidopsis thaliana*) and human tumor cell lines. We have also investigated the capability of CdS QDs to adsorb human blood plasma or cell lysate proteins (yeast or tumor cell proteins) with two-dimensional gel electrophoresis and mass spectrometry identification (MALDI-TOF). In conclusion, our results provide new insights into the mechanisms of toxicity of metal-based nanomaterials.

Session 2A Toxicology and human health risks

Surface reactivity of CuO NPs is responsible for the early oxidative damages to A549 cells: a Trojan-horse independent mechanism

*Elisa Moschini (University of Milano Bicocca)**

Paride Mantecca (University of Milano Bicocca)

Abstract: Background: it has been demonstrated that CuO NPs are highly cytotoxic for the most of mammalian cells. The classical Trojan horse mechanism is retained to be the driver of cell death mainly after long exposure periods. This work aims to demonstrate that CuO NPs may have specific cell reactivity in the first phases of exposure independent from intracellular ion dissolution.

Methods: CuO NPs with similar primary size but different crystallinity and extracellular ROS production (Perelshtein et al., 2014) were administered to A549 cells as model for human toxicity.

After assessing of cell viability SH- oxidation and protein carbonylation were monitored by immunocytochemistry and immunoblotting. Electron microscopy techniques were used to investigate cell-particle interactions.

Results: all NPs induced very early oxidative stress leading to a significant cell viability decrease after 3-6h of exposure. This effect was more pronounced for semi-crystalline CuO NPs and was independent from extra- and intra-cellular copper release although particles were detected both on cell surface and in cytoplasm already after 1h of exposure.

Conclusions: CuO NPs induce very early cell oxidative responses related to the specific NP surface reactivity, with semi-crystalline CuO NPs displaying the higher cytotoxicity.

Since CuO-based NMs have been suggested as powerful biocidals a better characterization of the reactions at the bio-interfaces may help nanotechnologist in the safe-by-design synthesis of new antimicrobials.

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Session 2A Toxicology and human health risks

Nanotechnologies and Sustainability in the fields of Architecture and Preservation of Cultural Heritage

*Federica Fernandez (University of Palermo)**

Abstract: Nanotechnologies allow today many applications for building construction and cultural heritage preservation, through the availability on the market of smart materials, revolutionizing the traditional methods and techniques. These appear as groundbreaking and promising tools, being able to improve the performance of traditional building materials, like concrete, steel and glass. In particular, the several applications of nanotechnologies in the field of conservation of cultural heritage are transforming old procedures for intervention, overcoming the major faults characterizing some of the traditional products currently used, allowing a more reliable and sustainable preservation of artifacts by the use of non-toxic and environmentally friendly treatments.

This contribution presents the state of the art of the major nanostructured products for building construction and cultural heritage preservation sectors, illustrating the main characteristics that make these products more sustainable. The increased performances, as improved strength and durability of materials are magnified also considering the reduction of the environmental footprint of the built environment throughout the efficient use of resources. Finally, this contribution underlines that, even if these nanomaterials are contributing to a significant change in our life, we must ensure that the potential risks are identified and controlled, through developing new appropriate standards and codes for their application.

Session 2B Environmental exposure, release & fate

Nanomaterial Fate and Exposure Research: Where we are now and where we need to be to model environmental exposure

*Greg Lowry (Carnegie Mellon University)**

*Bernd Nowack (EMPA)**

Abstract: A decade of research on nanomaterial fate and exposure has led to greater understanding of the environmental fate of nanomaterials, their potential risks (and benefits), and an overall better understanding of the role of nanophase materials in environmental processes such as nutrient cycling. This research has also led to a better understanding of how the system complexity makes predicting nanomaterial behaviors challenging, and has identified the need for new tools and approaches to quantify and characterize nanomaterials in situ. Despite these advances in knowledge, there remains a gap between fundamental data collection and the data needs for developing and parameterizing models for predicting environmental flows, fate and exposure. This talk will summarize on the one hand the advances in understanding nanomaterial behavior in complex environmental systems made over the past decade, and will highlight the critical areas of research needed to continue advancing our understanding. On the other hand, it will present where we are standing with respect to understanding the actual flows of nanomaterials to the environment and possibilities to model their environmental fate. The future lays in a more intimate collaboration between experimental and modeling work and we will be plotting a path towards better coupling of experimental work and model development and validation.

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Session 2B Environmental exposure, release & fate

Nanomaterials in a perspective of effects on ecosystem services and ecological risk

*Janeck J. Scott-Fordsmand (Aarhus University)**

Teresa Fernandes (Heriot-Watt University)

Richard Handy (Plymouth University)

Jose M. Navas (INIA)

Dick T.F.M. Roelofs (VU University Amsterdam)

Kerstin Hund-Rinke (Fraunhofer Institute for Molecular Biology and Applied Ecology)

Monica J.B. Amorim (University of Aveiro)

Abstract: The overall objective of this talk is to provide an overview of the tools that enables us to identify the long-term consequences of NMs on important ecosystems services. The focus will be on identifying tools for the environmental effects of long-term and repeated exposure to NMs as in production, in use and in wastes. There will be a special focus on ecosystems functions and species and on how rapid (including high throughput) tools can be used to provide information on potential long-term environmental consequences and impacts on services. The presentation will cover approaches for ecosystem services covering all media. It will also be discussed how such tools can be using on a probabilistic risk assessment. Within this talk we will also report the progress of the work performed within the SUN project.

Session 2B Environmental exposure, release & fate

A Dynamic Probabilistic Material Flow Modeling Method for Environmental Exposure Assessment of Engineered Nanomaterials

*Nikolaus A. Bornhoft (EMPA/University of Zurich)**

Lorenz M. Hilty (University of Zurich)

Bernd Nowack (EMPA)

Abstract: Material flow modeling constitutes an important tool to predict and understand the flows of materials through the technosphere into the environment. We present a new Dynamic Probabilistic Material Flow Assessment (DPMFA) method, combining dynamic material flow modeling with probabilistic modeling. The new method represents a significant step forward compared to established MFA or dynamic MFA methods because it allows to consider a large range of different uncertainties for all relevant model parameters. The modeler has the free choice to use distributions functions, or discrete data to describe the uncertainty of all parameters, allowing to make full use of the available data with varying degree of uncertainty. We implemented the method as simulation framework in Python to support experts from different domains in the development of their application models. In the talk we first introduce the DPMFA method and the simulation framework. Then we show an exemplarily application of the framework to predict current and future environmental concentrations of carbon nanotubes for Switzerland.

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Session 2B Environmental exposure, release & fate

Fate of fullerenes (C60) during peracetic acid (PAA) post disinfection of treated alum-enhanced combined sewer overflow (CSO) primary treatment

*Haitham Elnakar (University of Alberta)**

Mohamed Gamal El-Din (University of Alberta)

Abstract: Discharging combined sewer overflows (CSOs) directly or with minimal treatment into water bodies could elevate the concentrations of nanomaterials (NMs) in the receiving environment as a result of their extensive use in wide range of products. Among different NM types, fullerenes (C60) have been shown to pose risks on humans and aquatic organisms. Consequently, their fate and removal pathways should be assessed, and cost-effective and simple strategies to reduce their concentrations prior to their release should be developed. The objective of this study was to examine, for the first time, the fate of C60 in CSO when the effluent of alum-enhanced CSO primary treatment was disinfected with peracetic acid (PAA). A factorial design jar tests were firstly conducted to determine the optimum C60 removal conditions in terms of applied alum dose, mixing conditions and pH. At optimum coagulation conditions, the water was subjected to a post disinfection using PAA, and the effect of different PAA doses and contact times on the C60 transformation was investigated. The removal of C60 increased with the increase of contact time and applied PAA dose. It was also observed that acetic acid formation affected C60 detection. A further elucidation of the reaction mechanism and reaction by-products is underway.

Session 2B Environmental exposure, release & fate

Dynamic Probabilistic Modelling of Environmental Emissions of Engineered Nanomaterials

*Tian Yin Sun (EMPA)**

Nikolaus A. Bornhoft (EMPA/University of Zurich)

Bernd Nowack (EMPA)

Abstract: Currently little is known about engineered nanomaterial (ENM) concentrations in the environment. In 2009, we reported the first environmental concentrations for different ENM by applying probabilistic material flow modelling, which was recently updated to yield more comprehensive and up-to-date environmental concentrations of ENM. However, the used models are static and do not consider time-dependent processes. We present here results from a dynamic model that advances the estimation of environmental emissions and concentrations in two ways: first, instead of considering only one year's input and distribution, it takes a realistic time frame as the temporal boundary of the system and tracks the flows over many years. Second, rather than simply assuming that all ENM are released to waste streams and environmental compartments in the same year when they entered the system, time dependent ENM release from products are taken into account. This presentation focuses on the first results obtained for nano-TiO₂, nano-ZnO, nano-Ag and CNTs. We combined the available information of ENM input, product life-time and release dynamics and were able to predict a 'real' environmental emissions and concentrations of ENM, especially the accumulated ENM concentration in sinks such as soils and sediments.

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Session 2B Environmental exposure, release & fate

Implications of using inappropriate fate descriptors for engineered nanoparticles

*Antonia Praetorius (University of Vienna)**

Frank von der Kammer (University of Vienna)

Thilo Hofmann (University of Vienna)

Abstract: There has been a lot of debate in recent years regarding appropriate fate descriptors for engineered nanoparticles (ENPs), needed to predict ENP concentrations and transport in different environmental compartments. It is tempting to simply apply concepts for conventional organic pollutants, such as the use of equilibrium partition coefficients (e.g. K_{ow} , K_d) in fate and risk assessment of ENPs. However, due to their fundamentally different properties compared to organic chemicals, equilibrium partition coefficients lack a fundamental physical definition for ENPs and a fate assessment based on such coefficients is essentially meaningless. Here we present a few short case studies to demonstrate the implications of using any sort of ill-defined distribution coefficient in fate predictions for ENPs. We demonstrate the results of using operationally defined partition coefficients in different types of model predictions to exemplify why such coefficients cannot be used in the same universal manner as equilibrium partition coefficients are used in fate models for organic contaminants. Currently, model validations with field measurements of ENP concentrations in complex environmental matrices are not yet feasible, making it particularly important to carefully design environmental fate models for ENPs based on a strong theoretical understanding of the underlying processes to avoid making meaningless model predictions.

2C Industrial decision support tools

Conceptual framework for Sustainable Nanotechnologies Decision Support System (SUNDS)

*Vrishali Subramanian (Ca' Foscari University of Venice)**

Ineke Malsch (Malsch TechnoValuation)

Martin Mullins (University of Limerick)

Danail Hristozov (Ca' Foscari University of Venice)

Abstract: Nano-innovation can be impeded by significant knowledge and data gaps in the Environmental Health and Safety effects of Engineered Nanomaterials. The European Commission has funded a project on sustainable nanotechnology (SUN, <http://www.sun-fp7.eu/>) that aims to build tools to assess ecological and human health risks, environmental impacts, risk management measures and benefits of nano-enabled products. These tools will be integrated within an overarching decision framework and support tool for Sustainable Nanotechnology to support the selection of risk management alternatives (e.g. safety by design technological alternatives, personal protective equipment) and benefit-risk evaluation of nano-enabled products. Design of the SUN Decision Support System (SUNDS) framework is also supported by a comprehensive elicitation of user needs from the industry, regulatory and insurance sector. The framework will be implemented in a user-friendly modular software and will be tested on the SUN case studies. We present SUNDS conceptual framework and user needs with respect to SUNDS features.

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2C Industrial decision support tools

LICARA - guidelines for sustainable competitiveness of nanoproducts

*Claudia Som (EMPA)**

Esther Zondervan-van den Beuken (TNO)

Toon van Harmelen (TNO)

Roland Hischier (EMPA)

Bernd Nowack (EMPA)

Ingrid Hincapie (EMPA)

Dominic Notter (EMPA)

Harrie E. Buist (TNO)

Wouter Fransman (TNO)

Jörg Güttinger (TNO)

Abstract: Small and medium sized enterprises (SMEs) often lack resources to do a detailed assessment of benefits and risks of a new nanoproduct along its life cycle. The EU FP7 project LICARA has elaborated guidelines for developing safe and sustainable nanoproducts in order to support the decision making of SMEs. The guidelines intend to facilitate the communication within the value chain. SMEs should be supported to document their efforts for best practices and to communicate with their suppliers, clients, consumers and the authorities. The first part of the LICARA guidelines provides a stepwise approach and raises questions that can be answered qualitatively with a relatively low effort. It provides some background information that is currently only available as fragments in scientific literature but not in a condensed form. The second part describes the accompanying tool LICARA nanoSCAN, which enables SMEs to take a transparent more in-depth look by conducting an assessment in a semi-quantitative way. The third part provides information for further steps. The guideline is based on the scientific work of the research institutes TNO, Empa, RAS and the experiences of the private sector companies NCB, SNT, Fresco, Nanothinx and AGPYME, which have been partners in the consortium of LICARA.

2C Industrial decision support tools

Processing Nanoparticles in Suspension of High Solid Concentration: On-line Characterisation and Process Modelling

*Xue Z. Wang (University of Leeds)**

Ceyda Oksel (University of Leeds)^p

Abstract: Manufacture of nanometre particulate form products in suspensions is becoming increasingly important to the pharmaceutical, speciality chemical, and functional material industries. For instance, nano-processing is now used as an effective drug-delivery method for solid form hydrophobic pharmaceuticals due to the dramatically increased drug solubility and bioavailability at nano-scale. The biggest challenge to nano-processing under industrial conditions has been highlighted as the difficulty in achieving consistency in product quality as characterised by particle size distribution. In this work, we report investigation on on-line characterisation and process modelling techniques that can be applied under industrial operational conditions. The research on on-line sensing is based on acoustic spectroscopy for real-time particle sizing. The work will tackle the key challenge posed by multiple scattering and particle-particle interactions, which are known to be the cause leading to incorrect measurement at high solid concentrations. High solid concentration is not only the economically viable range for commercial manufacture of nanoparticles (a much larger reactor would be required to process the same amount of particles in low concentration), but also technically essential for producing ultra-fine particles for many processes. The on-line real-time measurement will provide invaluable data to the

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development of process models using population balance equations. The focus will be on quantitatively deriving models for particle breakage and aggregation to be used in the population balance equations, as well as intelligent interpretation of the data to improve the qualitative understanding of the process. The process chosen for investigation is wet nano-milling, a very important operation for processing nanoparticles in the pharmaceutical, agrochemical and materials industries.

Session 2C Industrial decision support tools

Broadening our view on nanomaterials: highlighting potentials to contribute to a sustainable materials management in preliminary assessments

*Henning Wigger (University of Bremen)**

Till Zimmermann (University of Bremen/ ARTEC)

Christian Pade (University of Bremen)

Abstract: Apart from completely novel functionalities, the utilization of nanomaterials (NMs) holds great promise for increasing the performance and efficiency of products and processes. In doing so, they are also expected to be more sustainable in that they may allow for products and processes that can provide better services using less material and energy. However, whether or not NMs do in fact contribute sustainable development still remains a matter of debate. While a relatively high number of risk assessment studies have revealed some of the toxicological and ecotoxicological repercussions of NMs, other sustainability related issues have so far received comparatively little attention. One of these issues refers to the sustainability implications of material use, such as environmental impacts of materials supply, resource depletion, or material criticality. Here, we argue that an adequate assessment of NM-based innovations calls for an inclusion not only of human health and environmental risks but also of aspects related to sustainable materials management. Recognizing the inherent complexity of sustainability issues as well as the difficulties of meeting data needs in early innovation stages, we propose a prospective and preliminary framework to assess the potential benefits and risks of NM-based innovations. We demonstrate the framework's practicability and usefulness in decision-making contexts by applying it to four in-depth case studies of specific NM-based innovations. Also, we point to some methodological issues that may need consideration in the further improvement of the framework.

Session 2C Industrial decision support tools

Anticipatory Ethics and Governance [AEG]: a Jurisprudential approach

*Karena Hester (University of Limerick)**

Martin Mullin (University of Limerick)

Finbarr Murphy (University of Limerick)

Abstract: Nanotechnology (NT) - the deliberate and purposeful design production use and manipulation of nanomaterials encompasses disciplines including but not limited to chemistry, physics, material sciences, engineering, information technology, biotechnologies. While there is significant uncertainty in relation to the possible risks of the consequences of NT, there is significant certainty that NT offers indisputable convenience and efficiencies in the context of consumer products; it offers enormous potential benefits in environmental remediation and in the rapidly evolving field of "nanomedicine" – in the areas of diagnostics, targeted drug delivery systems and disease monitoring. In this context it can make a valuable contribution to quality of life and well-being, particularly in developing countries (with an estimated population of 6-7 billion people) in relation to which close correlation between NT applications and six of the eight UNs millennium development goals has shown the capacity of NT to contribute to serious health, environmental and social issues. However, on the risk side, concerns have been raised

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in relation to the unknown risks of the potential hazard and harm to human health and safety, the environment and the earth's biosphere. Risk requires oversight in the form of regulation, governance or a hybrid of both but regulation requires information and more certainty of scientific information than is presently available. To that end, NT risk and the lack of scientific certainty place regulators in a dilemma. NT presents regulators and policy makers with a paradigmatic "Wicked problem". In the EU, regulation is largely framed on the basis of the precautionary principle— in itself an ethical concept underpinned by utilitarian consequentialism. For many reasons the precautionary principle is not an effective regulatory instrument yet precaution can be traced as a consistent thread through EU legislation which applies to NT – REACH, food, cosmetics, pharmaceuticals, occupational safety, waste and biocides. Save for novel foods, cosmetics and biocides, EU regulation is not NT specific and is based on risk assessment - theoretically straightforward but difficult in reality because of the extent of uncertainty surrounding risk of harm. In fact there is a view that for many reasons it is too soon to regulate NT effectively. Furthermore, the technology has already outpaced the legislation and it is possible that the regulation can be avoided or at least circumvented so as to be rendered inapplicable and outside the scope. All of this presents an opportunity to develop alternative approaches to oversight largely based on voluntary governance frameworks which are not dependent on scientific certainty and which shift the focus from risk assessment and analysis to risk minimization and mitigation. In the NT context there is scope for framing "soft law" governance mechanisms based on deliberative democracy and distributive and procedural justice which can be regarded as an exercise in ethical due diligence. An alternative approach focuses on the voluntary assumption of responsibility, on participation, deliberation, reflexivity and the future. The approach posited is grounded on jurisprudential theories of distributive and procedural justice incorporating John Rawls' theory of overlapping consensus and model of wide reflective equilibrium with the ultimate goal of the alignment of NT governance with the thinking of the "Law of People". It is anticipatory, flexible, adaptable and evolutionary. Because the acceptance of risk is a societal consideration the approach is multi-disciplinary forward looking and future care oriented which encompasses a broad stakeholder base.

Plenary Lecture 3

Regulatory and Policy Initiatives in the US and EU

Lynn L. Bergeson (Bergeson & Campbell, PC)

Abstract: This presentation would review and discuss key regulatory and policy developments in US and EU law. The focus would be on developments that are or could be pursued to foster the utilization of nanotechnology as a sustainable alternative to more conventional technologies. In a perfect world, an EU representative would co-present and give the EU side of the equation.

3A Safer by design products, production and processes

Sustainable Nanocatalysts for Fuel Cells and Splitting Water: Metal-Free, Heteroatom-Doped Carbons and Noble Metal-Free Oxides

*Tewodros (Teddy) Asefa (Rutgers University at New Brunswick)**

Abstract: The lack of sustainable and efficient catalysts for many renewable energy applications (e. g., fuel cells and water splitting) and the unabated negative environmental impacts of fossil fuels remain among the most pressing issues facing the world today. In this talk I will discuss my research group's recent efforts on the synthesis of heteroatom-doped metal-free or noble metal-free nanoporous and mesoporous carbon, metal oxide and carbon/metal oxide hybrid materials that exhibit high catalytic and electrocatalytic activity for reactions such as oxygen reduction reaction, hydrogen evolution reaction, and hydrazine oxidation— reactions that are relevant to fuel cells, water splitting, renewable energy, and so on. The catalytic activity of some of these materials is comparable or better than platinum-based catalysts, conventional catalysts that are widely used for such reactions but are deemed unsustainable due to their scarcity and high cost. Our findings, which defy the conventional paradigms, are also important for fundamental studies in the current state-of-the-art of catalysis that rely only on metallic systems. In the last part of my talk, I will describe novel design and “nanostructuring” approaches for a series of core-shell nanostructured materials with efficient catalytic or electrocatalytic activities for water splitting, hydrogen evolution and oxygen reduction reactions.

Session 3A Safer by design products, production and processes

Nanomaterials and Nanotechnology Firms in Europe: A Typology

*Anthony Carroll (University of Limerick)**

Martin Mullins (University of Limerick)^p

Finbarr Murphy (University of Limerick)

Abstract: Despite the widespread use of nanomaterials and nanotechnologies, little is known about the characteristics of the firms that comprise the industry. For instance, despite many studies opening with forecasts of a rapidly evolving industry with projected revenues of billions of euro, the industry's boundaries are not clearly delineated. By virtue of dealing with materials or technologies on a nanoscale, a wide range of firms, from those that produce nanoscale thin film coatings for semiconductors to those that sequence DNA, are seen, by some academics at least, to be part of the same industry. Furthermore, much of the previous work that has attempted to characterize such firms has depended on small-sample surveys with their associated self-reporting and non-response biases. This is problematic because, in order for regulators to regulate, insurers to underwrite risk, and financiers to provide capital, they must first have a deep knowledge of the industry in which they are involved. To address this shortcoming, this study describes the industry's typology in Europe. Using on-line databases and resources, we identify 517 European firms involved with either nanomaterials or nanotechnologies. Using manual searches of these firms' websites and public disclosures, we characterize each firm into one of six categories: Analysis, Bioanalysis, Drug Delivery, Electronics, Energy, and Materials. However, the operations of seemingly similar firms in each category can vary widely. For instance, while some of the 'Energy' firms manufacture photovoltaic cells, others manufacture ultracapacitors and lithium ion batteries. Moreover, such firms could ostensibly be categorized under the 'Electronics' heading. This has broader implications because it highlights the difficulties that regulators, insurers and capital providers have in evaluating the idiosyncratic risk that each nanomaterials or nanotechnology firm poses. We also find that the majority of these firms are privately owned, venture capital funded, and have less than 50 employees. This too has implications, particularly for regulators, as their actions could potentially have an adverse impact on what is evidently still a nascent, emerging industry.

Session 3A Safer by design products, production and processes

SANOWORK: towards a "Safety by Design" management of nanomaterials

*Simona Ortelli (ISTEC-CNR)**

Camilla Delpivo (ISTEC-CNR)

Anna Luisa Costa (ISTEC-CNR)

Abstract: The growing importance of engineered nanomaterials (ENMs) and their applications justifies the European successful promotion and growth of a nano-safety research. It is widely accepted that material designers, engineers, health and safety professionals, business leaders, should converge efforts to develop "Safety by design" (SbD) tools and implementing safer manufacturing processes. The approach followed by the EU collaborative project, SANOWORK, is in this direction. The main goal of Sanowork project has been to promote safe occupational exposure scenarios by developing preventive risk management measures and evaluating them in terms of RISK and expected PERFORMANCES. The results has provided inputs for a COST-BENEFIT analysis and the development of a RISK INSURANCE MODEL exploitable by industrial sectors involved. Five risk remediation strategies based on a SbD approach have been developed and integrated within the processing lines. The Sanowork approach has been applied to a "representative" pool of nanomaterials: ZrO₂, TiO₂ and Ag nanoparticles; CNTs; polyamide and TiO₂ nanofibers. The proposed strategies aimed to mitigate occupational risk by decreasing adverse health hazard and/or emission potential of nanomaterials, setting back processes of transport to the point of entry. The cooperation with industrial key partners has guaranteed an accurate exposure assessment in the workplace.

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Session 3A Safer by design products, production and processes

Assessing the potential risks of silver nanoparticles in antimicrobial applications, using miniaturized flow field-flow fractionation and multi-angle light scattering

*Valentina Marassi (University of Bologna)**

Anna Luisa Costa (ISTEC-CNR)

Barbara Roda (byFlow srl)

Abstract: Colloidal silver nanoparticles are known for their antimicrobial applications in everyday life items, and their use in commercial products is increasing; to investigate how and if nanoparticles may present harm for the environment and organisms, a characterization of their behavior in environmental/physiological media is required besides size, shape, activity and stability assessment. Hyphenation of multiangle light scattering (MALS) detection with size-based separation methods presents a multidimensional platform that can enhance accuracy for analysis of complex NPs samples, and Hollow-fiber flow field-flow fractionation (HF5) is particularly suited for this task. In HF5, separation occurs between species with different hydrodynamic radius. MALS detection, on the other hand, allows for the calculation of particles' gyration radius, which depends on particle compactness. Particles' shape is determined correlating these values.

We developed HF5-UV-MALS methods able to study dispersed AgNPs in aqueous media to isolate silver nanoparticles for size distribution analysis, identify aggregation phenomena, separate unbound constituents from the functional NPs, and correlate NPs size with their spectroscopic properties. We have tested new methods for analysis of metal release through fiber filtration to improve full characterization of metal-based nanoparticles, in order to study both their functional effectiveness and potential hazards.

Session 3B Ecotoxicology, effects on ecosystem services & ecological risks

Ecotoxicological effects of multi walled carbon nanotubes

*C. Piller (Tel Aviv University)**

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Abstract: Now-a-days the need for the manufacturing of engineered nanomaterials increases due to their performance, efficiency and decrease of total weight in the applications they are used. However, not always large scale manufacturers or even small scale pilot lines established in regional laboratories follow regulations/limitations for the disposal of engineered nanomaterials waste. Consequently, there is a great possibility of polluting water that will eventually result in the effect on ecosystems micro and macro-organisms. In this study we will present the effect of carbon nanotubes (CNTs), one of the most widely studied engineered- nanomaterial on the water fleas, unicellular algae some macrofoulers. CNTs were synthesized via a thermal chemical deposition process, characterized and functionalized with different end groups to render them less toxic. CNTs length was measured ~5 µm and diameter ranged between 60-100 nm. Functionalization with different surfactants was conducted in order to render CNTs dispersal in polar and non-polar solvents and their effect on living organisms was assessed so as to estimate the potential effect in ecotoxicity and environment. Acknowledgements: This research is supported by the EU FP7 Project "Low-toxic cost-efficient environment-friendly antifouling materials" (OCEAN) under Grant Agreement no. 612717.

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Session 3B Safer by design products, production and processes

The GUIDEnano strategy for nanomaterial environmental hazard assessment along the life cycle

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Julia Catalán (Finnish Institute of Occupational Health)

Socorro Vázquez-Campos (LEITAT Technological Center)

Claus Svendsen (NERC Centre for Ecology & Hydrology, Molecular Ecotoxicology)

Abstract: GUIDEnano aims at developing an interactive web-based Guidance Tool to support the risk assessment and risk management of a nano-enabled product. A first step will be to assess the possibility to use existing hazard assessments for similar materials, by assessing similarity between the exposure-relevant and the already tested nanomaterials (NMs). This will be done by using a set of predefined read-across criteria that will lead to a similarity score for each property evaluated. As a second step, in cases where the exposure-relevant material is not sufficiently similar to any of the previously assessed materials, the Tool would base the hazard assessment on individual studies available for the NM of interest. Each individual study would be evaluated for two aspects: its reliability and the similarity of the tested NM to the exposure relevant NM. Within the reliability concept, we include the combination of the Klimisch score and a specific nano score. A minimum score for these two aspects will be needed to use such test data for the derivation of the final predicted non effect concentration (PNEC) value and, in such cases, the score will also inform on the uncertainty around it. A third and final step, the use of general categories of NMs and associated default hazard values is considered.

Session 3B Ecotoxicology, effects on ecosystem services & ecological risks

Phytotoxicity of carbon nanotubes in soybean is associated with disturbances of zinc homeostasis

*Olga Zaytseva (University of Hohenheim)**

Günter Neumann (University of Hohenheim)

Abstract: The effect of short-term seed treatments with multi-walled carbon nanotubes (CNTs, 0 – 500 µg seed⁻¹ during 36 h) on germination and seedling development of soybean was studied. CNTs decreased speed of the water uptake by soybean seeds and therefore reduced imbibition damages, which finally improved germination rate. However, at 8 days after sowing and even after 23 days of growth on a calcareous soil, plants developed from seeds treated with CNTs, showed stunted growth and poor fine root development associated with zinc (Zn) deficiency. The growth of affected plants was recovered by foliar applications of 0.5 mM ZnSO₄ or by cultivation in nutrient solution. Since Zn is an important co-factor for antioxidant enzymes, stunted plant growth in response to Zn limitation has been related to excessive oxidative degradation of auxin as growth hormone. We hypothesize that CNT seed treatments may affect re-mobilisation of Zn seed reserves, leading to the development of Zn-deficient seedlings with stunted root growth and lacking the ability to acquire sparingly soluble Zn forms in soils but with restoration of normal growth by external application of soluble Zn.

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Session 3B Ecotoxicology, effects on ecosystem services & ecological risks

Accumulation of engineered nanoparticles in plant foods: Nutritional bioaccessibility and dietary exposure risks

*Stephen D. Ebbs (Southern Illinois University)**

Xingmao Ma (Southern Illinois University)

Jason White (Connecticut Agricultural Experimental Station)

Abstract: The increase in the production of engineered nanomaterials (ENMs) has prompted concerns about their environmental release into and their impact on human health. Consumption of plants that have come in contact with nanomaterials is the most likely route by which humans could be exposed. Collaborative study of ENM accumulation in plants is underway with research efforts focused on an array of belowground and leafy vegetables. One aspect of this research is focusing on the transport of various ENM into plant tissues. The accumulation data from these experiments is also being used to develop dietary intake models to relate that accumulation to the potential impact resulting from consumption of those plant tissues. Models based on a series of experiments with the accumulation of CuO, ZnO, or CeO₂ in carrot have been completed and include comparative data from plant exposed to the corresponding ions of each ENM. Additional modeling is underway for lettuce and sweet potato. A physiologically-based extraction test is being applied to assess the release during the gastric phase of simulated digestion. The goal of these efforts is to provide a comprehensive picture of the food safety risk posed by these ENMs in these plant foods.

Session 3B Ecotoxicology, effects on ecosystem services & ecological risks

Mechanisms of response to NMs in soil invertebrates – integrating from gene expression to organism effect and AOPs

*Mónica J.B. Amorim (University of Aveiro)**

Susana I.L. Gomes (University of Aveiro)

Janeck J Scott-Fordsmand (Aarhus University)

Abstract: High-throughput gene expression tools can help understanding the mechanisms of toxic-mediated responses. Further, one of the main aims is to establish the link between alterations in macromolecules (genes, proteins) and their biological implications at higher levels (reproduction). Such data can be integrated via Adverse Outcome Pathways(AOPs) approach, and provide input towards a more knowledge based risk assessment. In the present study we investigated the mechanisms of toxicity for Cu (copper) and Ag (silver) materials using the high-throughput tool for the soil worm *Enchytraeus crypticus* (Oligochaeta), a 4x44K custom Agilent microarray. Testing was done based on reproduction effect concentrations (EC₂₀, EC₅₀) using 3 and 7 days of exposure. The materials included CuNP, Cu nanowires, Cu aged (80 years contaminated field) and Cu salt plus AgNP (non coated and PVP coated), AgNM300k (dispersed) and Ag salt. Results indicated specific mechanisms of response for the different materials tested. Cu-salt exposure affected mechanisms related with calcium homeostasis and activated the chemosensory system of the enchytraeids. Energetic metabolism was affected differently depending on the copper forms. For Ag, results showed that one of the materials caused a more differentiated transcriptomic profile than the others. Commonly and across all Ag forms were the effects on cell cycle control associated with impairment of DNA repair mechanism. The study of gene expression pointed at differences in gene responses that would had been absent via the standard methods alone. The AOPs approach is a promising means to overview effects in an integrated flow.

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Session 3C Educational & curriculum in nanotechnology

Inclusion of Sustainability Aspects in Technician Education Programs

Deb Newberry

Abstract: Sustainability is acknowledged to consist of three segments; economic, environmental and societal. The environmental aspect encompasses in many cases the technology and science of nano materials and the interaction with biological systems and the surrounding environment. The 2 year nanotechnology program at Dakota County Technical College encompasses many aspects of nanotechnology (electronics, materials and biotechnology) and also includes aspect of sustainability in multiple courses. And, rightfully, a substantial portion of nanotechnology based educational content focuses on the technical aspects of nanoscale phenomena. This presentation will address the remaining two segments of sustainability and discuss how economic and societal impacts of nanotechnology are woven into traditional technical content through case studies, experiments, and activities. Case studies presented focus on coating materials for aquatic applications and functionalized nanoparticles for disease treatment and include regulatory and material cost considerations, risk assessments and failure modes effects analysis.

Session 3C Educational & curriculum in nanotechnology

The Virginia Tech Interdisciplinary Graduate Education Program

Peter Vikesland (Virginia Tech)

Nina Vance (Virginia Tech)

Abstract: The Virginia Tech Sustainable Nanotechnology Interdisciplinary Graduate Education Program (SuN-IGEP) is a cross-university effort to promote interdisciplinary research in the general area of Sustainable Nanotechnology. This presentation will discuss the successes and challenges of this program, which provides financial support for a number of Ph.D. students with the goal to support development of expertise in sustainable nanotechnology. This presentation will discuss the central educational and research tenets of the SuN-IGEP effort.

Session 3C Educational & curriculum in nanotechnology

Learning from nature: biomimicry in nanotechnology education

*Mehlika Ayla Kiser (Catalan Institute for Water Research)**

Lluís Corominas (Catalan Institute for Water Research)

Ignasi Rodríguez-Roda (Catalan Institute for Water Research)

Abstract: Over the 3.8 Gyr since life is believed to have appeared on Earth, components of the natural world have evolved to function effectively and persist. Ecosystems are therefore rich sources of information and fundamental models of successful, sustainable strategies from which we can learn. Biomimicry is the study and imitation of nature's designs and processes to solve human problems and is a core concept for sustainability. Several nano-based innovations have been inspired by nature, such as green synthesis techniques for nanomaterials, water-purifying membranes, and scaffolds for tissue engineering. However, biomimicry is still an underdeveloped practice in nanotechnology. Teaching researchers and industries how to learn about and apply attributes of ecosystems to design and manufacturing will play an important role in the development of sustainable nanotechnology. Thus, curriculum and training for sustainable nanotechnology should include (1) learning and applying basic concepts of biomimicry; (2) practicing decision making; and (3) improving collaboration skills, particularly with biologists and ecologists. By actively integrating these elements into nanotechnology education, we can reduce the gap that currently exists between the principles of sustainability and the practical realities of developing and producing nanomaterials and nanodevices.

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Session 3C Educational & curriculum in nanotechnology

Nanotechnology education for secondary schools and university students: The employers perspective

*Albert Duschl (University of Salzburg)**

Bartlomiej Szafran (Akademia Gorniczo-Hutnicza, Poland)

Pawel Wojcik (Akademia Gorniczo-Hutnicza, Poland)

Bartlomiej Spisak (Akademia Gorniczo-Hutnicza, Poland)

Karen Griffin (University College Dublin, National University of Ireland)

Dorota Rutkowska-Zbik (Instytut Katalizy I Fizykochemii Powierzchni Polskiej Akademii Nauk)

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Thomas Zadrozny (NANO futures ASBL, Belgium)

Costas Kiparissides (Aristotle University of Thessaloniki & Centre for Research and Technology Hellas)

Olga Kammona (Centre for Research and Technology Hellas)

Frederick Ntow (Nanotechnology Industries Association)

Steffi Friedrichs (Nanotechnology Industries Association)

Moshe Talesnik (ORT Israel)

David Rosenberg (ORT Israel)

Yoel Rothshild (ORT Israel)

Ineke Malsch (Malsch TechnoValuation)

Abstract: The on-going FP7 project NanoEIS (www.nanoeis.eu) investigates European nanotechnology education practices and compares education contents to job skills that are in demand in the nanotechnology industry. Our studies show that industry expects to recruit experts in areas that are very poorly covered by university curricula, like health & safety, regulation & standardization, and environmental aspects. Nanotechnology studies focus strongly on classical disciplines and research-driven fields, which implies that students may not be really qualified in the skills that are in demand in the job market. Direct involvement of industry in university education is identified as the single most important factor that strongly facilitates a smooth transition from academia to industry. For secondary school education, the integration of nanotechnology has not yet developed an accepted standard. Islands of best practice have been identified which are implemented in very different ways, but the majority of secondary school students in all European countries is never in touch with nanotechnology at school. Better connections between schools, universities and industries would help to narrow the gap between education contents and job market needs, and could also help in reaching out to society at large.

Session 3C Educational & curriculum in nanotechnology

Empowering citizens in international governance of nanotechnologies

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Vrishali SUBRAMANIAN (Ca' Foscari University)

Elena SEMENZIN (Ca' Foscari University)

Danail HRISTOZOV (Ca' Foscari University)

Antonio MARCOMINI (Ca' Foscari University)

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Karena Hester (University of Limerick)

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Abstract: The international dialogue on responsible governance of nanotechnologies engages a wide range of actors with conflicting as well as common interests (c.f. Malsch, 2011). It is also characterised by a lack of evidence based data on uncertain risks of in particular engineered nanomaterials (c.f. IRGC, 2006). The SUN project aims to develop a SUNDS software decision support tool in order to strengthen collective decision making on sustainable nanomaterials. The design of the tool is based on three rounds of stakeholder engagement with industry, regulators and insurance company representatives. The present paper aims at deepening understanding of the collective decision making context at international level by reviewing recent discussions in different fields including sociological and political studies of international relations (e.g. Risse, 2002, Haas, 1992) as well as political philosophy and ethics (Habermas, 2011, Rawls, 1999, Kant, 1795). This analysis of current trends in international law making is taken as starting point for exploring the role a software decision support tool could play in multi-stakeholder global governance of nanotechnologies. These theoretical ideas are then compared with the current design of the SUNDS tool highlighting discussion points for further consideration.

Plenary Lecture 4

The quest for generating robust regulatory relevant data

Tom van Teunenbroek (*Ministry of Infrastructure and the Environment*)

Abstract: The NANoREG project is aimed at developing building blocks for the regulatory testing and assessing of Nanomaterials. To this end, the project will be “testing the tests” to, on one hand determine the most appropriate ways to assess the environmental, health and safety effects of nanomaterials, and on the other hand to generate information for read across and Safe by Design (SbD).

To achieve read-across, it is necessary to:

- * use the same test materials
- * harmonize the test method(s)
- * report specific measurements using the specific characterization methods
- * report the data in a specific format for final logging

By these four points we will all gain insight into the reliability of the specific test methods by comparing results, to be able to use the results of one task as input for another and last but not least, to generate a robust dataset on which the NANoREG project can build the conclusions and policy recommendations.

Session 4A Recycling & Waste Management

Waste management of ENM-containing solid waste in Europe

*Laura Heggelund (Technical University of Denmark)**

Alessio Boldrin (Technical University of Denmark)

Steffen Foss Hansen (Technical University of Denmark)

Abstract: Little research has been done to determine emissions of engineered nanomaterials (ENM) from currently available nano-enabled consumer products. While ENM release is expected to occur throughout the life cycle of the products, this study focuses on the product end-of-life (EOL) phase. We used the Danish nanoproduct inventory (www.nanodb.dk) to get a general understanding of the fate of ENM during waste management in the European context. This was done by: 1. assigning individual products to an appropriate waste material fraction, 2. identifying the ENM in each fraction, 3. comparing identified waste fractions with waste treatment statistics for Europe, and 4. illustrating the general distribution of ENM into incineration, recycling and landfilling. Our results indicate that plastic from used product containers is the most abundant and diverse waste fraction, comprising a variety of both nanoproducts and materials. While differences are seen between individual EU countries/regions according to the local waste management system, results show that all waste treatment options are significantly involved in nanowaste handling, suggesting that research activities should cover different areas. The results of this study may be used for the environmental and human health risk assessment of nanowaste, and to assist future regulatory and management decisions.

Session 4A Recycling & Waste Management

Flows of engineered nanomaterials through the recycling process in Switzerland

*Alejandro Caballero-Guzman (EMPA)**

Tian Yin Sun (EMPA)

Bernd Nowack (EMPA)

Abstract: The use of engineered nanomaterials (ENMs) in diverse applications has increased during the last years and this will likely continue in the near future. As the number of applications increase, more and more waste with nanomaterials will be generated. A portion of this waste will enter the recycling system, for example, in electronic products, textiles and construction materials. The fate of these materials during and after the waste management and recycling operations is poorly understood. The aim of this work is to model the flows of nano-TiO₂, nano-ZnO, nano-Ag and CNT in the recycling system in Switzerland. The basis for this study is published information on the ENMs flows on the Swiss system. We developed a method to assess their flow after recycling. To incorporate the uncertainties inherent to the limited information available, we applied a probabilistic material flow analysis approach. The results show that the recycling processes does not result in significant further propagation of nanomaterials into new products. Instead, the largest proportion will flow as waste that can subsequently be properly handled in incineration plants or landfills. Smaller fractions of ENMs will be eliminated or end up in materials that are sent abroad to undergo further recovery processes. Only a reduced amount of ENMs will flow back to the productive process of the economy in a limited number of sectors. Overall, the results suggest that risk assessment during recycling should focus on occupational exposure, release of ENMs in landfills and incineration plants, and toxicity assessment in a small number of recycled inputs.

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Session 4A Recycling & Waste Management

Nanoproducts: What is Actually Available to European Consumers?

*Steffen Foss Hansen (Technical University of Denmark)**

Laura Heggelund (Technical University of Denmark)

Aiga Mackevica (Technical University of Denmark)

Abstract: It remains unclear what is available in Europe when it comes to consumer products containing nanomaterials (NM), which hampers quantitative exposure assessment. To provide an overview of available nanoproducts, we have established The Nanodatabase (www.nanodb.dk), an online inventory of products claimed by manufacturers, importers, retailers, and web-shops to contain nanomaterials. The database currently entails almost 1400 products, 200 of which in the categories of cleaning and personal care. While including basic information about the product (e.g., name, NM used, location of NM in the product), a unique feature of the database is that it provides qualitative exposure/hazard evaluation of individual products based on the NanoRiskCat evaluation framework. Furthermore, the analysis section of the Nanodatabase website allows the user to do their own data sorting (product types, NMs used, number of products, etc.). While silver and titanium dioxide are the most used NMs, we could not identify the NM in more than 60% of all products. The presentation will furthermore include data on potential route of exposure to humans and the environment, results of the NanoRiskCat evaluation, distribution of the products according to their end-of-life fate and limitations of the database.

Session 4A Recycling & Waste Management

Stochastic fate analysis of engineered nanoparticles during release processes, e.g. in an incineration plant

*Fadri Gottschalk (ETSS)**

Tobias Walser (ETSS)

Abstract: A full-scale experiment in a modern waste incineration plant showed that even inert nanoparticles (nano-CeO₂) are successfully removed from the flue gas and transferred to the solid incineration residues. Predicting the fate of nanomaterials in incineration plants with models based on real measurements would reduce the immense efforts (time and resources) for real-scale experiments. A model for the ENP fate in incineration plants, based on the data of the nanoCeO₂-experiment is presented. We investigated all possible transfers and sinks of ENP throughout the incineration by linking ENP concentration measurements to the nanomaterial flows and retention times. The model also delivers information on the associated uncertainties and how they propagate through the incineration system. The model can be generalized to other ENP and also to other incineration plants. We show that the output of the measurements was consistent albeit relying on multiple measurement methods, and that a one day sampling period is sufficient to obtain an overview on the fate of nanoparticles in incineration plants. In addition to the dynamic results, a generalized steady state mass flow with transfer factors is provided and can be used for modeling purposes of CeO₂ or other nano sized metals with similar physic-chemical properties.

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Session 4B Toxicology and human health risks

NanoSAR: Structure Activity Model for the Toxicity of Nanoparticles

*Ceyda Oksel (University of Leeds)**

Cai Yun Ma (University of Leeds)

Xue Z. Wang (University of Leeds)

Abstract: There are increasing number of engineered nanomaterials (ENMs) that have to be hazard tested before they are allowed to be used in commercial and industrial applications. This requires new methodologies to be explored and implemented to rapidly and effectively screen and evaluate ENM toxicity. Data-driven models of nanostructure-biological activity relationships are becoming increasingly important as the hazard testing lags further behind innovation in nanotechnology. Although the use of non-testing quantitative structure-activity relationship ((Q)SAR) methods for predicting adverse effects of ENMs has gained more and more attention over the past several years, there exist a number of limitations that influence the quality and generalizability of nano-(Q)SAR models. This study reviews (Q)SAR-related nano-aspects, from nanostructure characterization to (Q)SAR modelling tools, in order to improve the understanding of the (Q)SAR modelling of ENM toxicity. It provides a critical assessment of previously published nano-(Q)SAR studies as well as the available nanostructure-nanotoxicity data. Moreover, the study aims to identify the issues that complicate the implementation of (Q)SAR approaches in nanotoxicology, in addition to the main challenges ahead. In conclusion, we believe that this study can provide valuable insights into the current status and future potential of (Q)SAR modelling in nanotoxicology.

Session 4B Toxicology and human health risks

Contribution to nanomaterials safety assessment: the need of integrating in vitro, in vivo and in silico strategies

*Maria João Silva (National Institute of Health Doutor Ricardo Jorge)**

Henriqueta Louro (National Institute of Health Doutor Ricardo Jorge)

José Maria Albuquerque (National Institute of Health Doutor Ricardo Jorge)

Teresa Borge (General-Directorate of Health)

João Lavinha (National Institute of Health Doutor Ricardo Jorge)

Abstract: Fundamental and application-driven research in nanotechnology is expected to boost nanoscience and innovation towards development of safe-by-design nanomaterials (NM). In this scenario, adding vast societal benefits, a multi-disciplinary approach to responsible innovation must be undertaken. Although the widespread use of NM, it is not clear whether they impact on environment and human health, on the long-term. Potential deleterious effects, e.g., genotoxicity that is intimately associated with carcinogenicity, have to be assessed using complementary in vitro and in vivo assays, nested within the conventional risk assessment paradigm and considering specific physicochemical properties of NM. In this study we present the testing strategy that was recently applied to the genotoxicity characterization of titanium dioxide nanomaterials in human cells and in an integrative in vivo model. The results supported the view that a thorough understanding of the relationship between the physicochemical properties, the behaviour of NM in biological systems and their mechanism of action is of utmost importance to predict their biological activity. In conclusion, the knowledge gap between nanoscience and hazard assessment has to be filled within a multi-disciplinary approach including experimental and computational components in an iterative process, towards an improved strategy for the safety evaluation of nanomaterials.

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Session 4B Toxicology and human health risks

Development of a robust method for measuring engineered nanomaterial toxicity and uptake using *Caenorhabditis elegans*

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Peter Wick (EMPA)

Abstract: Design and development of reliable cell-based nanotoxicology assays are important for evaluation of potentially hazardous engineered nanomaterials. Challenges to producing a reliable assay protocol include working with nanoparticle dispersions and living cell lines, and the potential for nano-related interference effects. We demonstrate the use of a 96-well plate design for a nano-cytotoxicity MTS cell viability assay. A detailed protocol and an inter-laboratory comparison are used to illustrate the variability of the assay with NH₂-polystyrene nanoparticles. Data on both the within and between laboratory system controls can be used to evaluate the largest sources of variability in the protocol. This study suggests that a high level of agreement between each of the laboratories can be achieved, but consideration of protocol details such as cell line ID, cell rinsing, media removal, and nanoparticle dispersion is critical to ensure comparability of nanocytotoxicity assays results.

Session 4B Toxicology and human health risks

Design and Development of Surface Modification and Synthesis Strategies to Reduce Toxicity of Nanoparticles

*Seda Keleştemur (Yeditepe University)**

Manolya Hatipoğlu (Yeditepe University)

Mine Altunbek (Yeditepe University)

Mustafa Culha (Yeditepe University)

Abstract: The aim of the study is to develop new modification and synthesis strategies to reduce the toxicity of nanoparticles (NPs) used in ink and pigment industry. Zinc oxide (ZnO) NPs, quantum dots (QDs) and silver nanoparticles (AgNPs) were selected NPs due to their high toxicity. Biocompatibility, stability in ink formulation, chemical suitability, cost and applicability are the main requirements for the selection of the materials for surface modifications. Plasma proteins; bovine serum albumin, fibrinogen

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and apo-transferrin were chosen as surface modifiers for ZnO NPs and glucose was selected as a model carbohydrate for QDs to reduce toxicity. The covalent binding of surface modifiers on ZnO NPs and QDs was verified by spectroscopic and gravimetric techniques to demonstrate the success of surface coverage. A comprehensive evaluation of cellular toxicity of pristine and modified NPs demonstrated the surface modification of NPs decreased the toxicity influentially. A safety by design approach was developed to reduce toxicity of AgNPs through modifying synthesis conditions. The influence of synthesis conditions of AgNPs on size and toxicity was also investigated and the synthesis conditions were found as effective as the size dependent toxicity.

Session 4B Toxicology and human health risks

Development of an initial Risk Assessment strategy within the GUIDEnano project

*Susan Wijnhoven (RIVM)**

Petra van Kesteren (RIVM)

Maria Luisa Fernandez-Cruz (INIA)

Juan J. Izquierdo (INIA)

Thies Oosterwijk (TNO)

Derk Brouwer (TNO)

Abstract: One of the main goals of work package 7 of the GUIDEnano project is to develop a risk assessment strategy for an NM-enabled product during its development and before introduction on the market. This risk assessment strategy is incorporated in the interactive web-based GUIDEnano Tool, which will guide the NM-enabled product developers (mainly industry) into the design and application of the most appropriate risk assessment and mitigation strategy for a specific product. The strategy will be evaluated with hypothetical and real case studies within the project. To develop the initial strategy to assess the risk of NMs, information on existing risk assessment methodologies was used, together with discussions with experts from inside and outside the project. The strategy can be divided in four main elements: 1. Input and information requirements (hazard and exposure assessment) 2. Risk assessment (calculation of a risk ratio and classification into three risk categories) 3. Follow-up actions (reduction of uncertainty, risk mitigation) 4. Output report. Currently, WP7 is working on a sensitivity analysis of the entire risk assessment process, as integrated in the Tool, to identify the key assumptions or uncertainties to be reduced throughout this process.

Session 4C Toxicology and human health risks

Evaluation of titanium dioxide nanoparticle fate and heteroaggregation in natural surface waters

*Danielle Slomberg (CEREGE)**

Jérôme Labille (CEREGE)

Patrick Ollivier (BRGM)

Abstract: As development of engineered nanoparticles (ENPs) continues to progress, determination of ENP fate and impact on the natural environment remains challenging, and new strategies utilizing environmentally relevant system compositions and ENP concentrations (i.e., µg/L range) are warranted. Herein, we evaluated the fate of titanium dioxide (TiO₂) ENPs in surface waters from a river (Rhône river, France) rich in mineral suspended particulate matter (SPM) and a lake (Cholet, France) containing high levels of natural organic matter (NOM). The TiO₂ ENPs were spiked into these waters and the ENP/natural suspended matter heteroaggregation kinetics and sticking efficiencies were determined. To elucidate the physico-chemical factors driving heteroaggregation, studies were also conducted in

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synthetic waters of comparable composition. Furthermore, pH, ionic strength, elemental composition, and SPM and NOM contents and compositions were assessed to identify the key contributors to ENP fate. The TiO₂ nanoparticles demonstrated a significant affinity for the mineral SPM, with rapid heteroaggregation and subsequent sedimentation of the resulting aggregates. However, heteroaggregation was less evident in the NOM-rich lake water. Together, these holistic data will serve in ranking potential ENP fate scenarios and assessing ENP risk within natural aqueous environments. Funded by the French ANR and the Swiss FOPH under ERA-NET SIINN NANOHETER.

Session 4C Toxicology and human health risks

Kinetics of Nanoparticles Release from Nanocomposites Exposed to Environmental Stresses

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Deborah Stanley (NIST)

Savelas Rabb (NIST)

Justin M. Gorham (NIST)

Lee L. Yu (NIST)

Tinh Nguyen (NIST)

Abstract: Nanocomposites are increasingly used in essentially every segment of the industry from consumer products to aerospace. Regardless the application, both the long-term performance of the composite itself and the fate of the nanomaterials in the matrix during the product's life cycle play a key role in the commercialization and uses of these nanocomposite products. The main reason for that is nanomaterials that were embedded in the polymer matrices may be released from the nanocomposites during their life cycles. Little data is available about the fate of free or embedded nanoparticles, how they may be released, and the quantity/composition/structure of the released particles throughout the product's life cycle. The goal of this study is to investigate the process and mechanism of particle release from nanocomposites under accelerated UV exposure. Specimens of a nanosilica composite were exposed to a well-controlled, accelerated UV environment, and the amount of nanosilica particles from the degraded surface were collected using a simulated rain process, and measured using inductively-coupled plasma optical emission spectroscopy as a function of UV exposure time at different temperatures. This result will be valuable for developing a kinetics model to predict the long term release of nanosilica from polymer nanocomposites when used outdoors.

Session 4C Toxicology and human health risks

Environmental fate of nanopesticides and exposure assessment

*Melanie Kah (University of Vienna)**

Anne-Kathrin Weniger (University of Vienna)

Thilo Hofmann (University of Vienna)

Abstract: Research into nanotechnology applications for use in agriculture has become increasingly popular over the past decade. Investigations into the environmental fate of nanopesticides remain scarce however, and the current state of knowledge does not appear to be sufficient for a reliable assessment to be made of the benefits and risks associated with nanopesticides. It is not clear for instance, whether current analytical methods, test protocols and exposure modelling approaches can account for novel "nano" properties of some nanopesticides. With the aim to address the knowledge gap, experiments were carried out on a series of polymer-based nanopesticides. The suitability of standard regulatory protocols to determine fate parameters in soils (OECD tests for sorption and degradation) was evaluated in the context of pesticide regulatory assessment in the EU. Discrepancies between free and

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nanoformulated active ingredient were also analysed based on the results obtained by more realistic experimental set up and from the characterization of the nanocarriers. Comparison with commercial formulations was also considered to distinguish nano-specific-effects from those related to already existing formulations. Overall, results serve as a useful basis to discuss the (in)adequacy of current protocols, and identify priorities for research.

Session 4C Toxicology and human health risks

Insights from a spatially and temporally resolved nanoparticle fate model

*Amy Dale (Carnegie Mellon University)**

Greg Lowry (Carnegie Mellon University)^p

Elizabeth Casman (Carnegie Mellon University)

Abstract: We introduce a spatially and temporally resolved mass balance model for sulfidized Ag NP and ZnO NP loadings to the James River Basin in Virginia. The model includes oxygen-, sulfide-, and temperature-dependent NP and byproduct (ion) transformations, oxic and anoxic sediment layers, and flow-dependent sediment transport. Although it has been generally ignored in NP fate models, surface runoff of land-applied biosolids accounts for roughly a quarter of NP stream loads in our model. Due to daily flow dynamics, NPs were also more mobile than anticipated in the stream, with only ~5-10% of the cumulative stream load remaining in the basin at the end of the simulation. Therefore, metals from NPs will accumulate downstream in estuarine or marine ecosystems. Spatially variable discharges and stream flows, control predicted environmental concentrations (PECs) in this model. Previous steady state models or those applying time-constant parameters and processes suggest peak PECs occur during low flows. We also observe peaks during high flows due to surface runoff. Unlike sulfidized Ag NPs, ZnO NPs rapidly dissolve. PECs never exceed USEPA water or sediment guidelines for Ag and Zn, suggesting low risk in this system at estimated current loading levels.

Session 4C Toxicology and human health risks

Thermal decomposition of nano-enabled products at their end of life and EHS implications

*Georgios A. Sotiriou (Harvard University)**

Dilpreet Singh (Harvard University)

Philip Demokritou (Harvard University)^p

Abstract: Proliferation of Nano-enabled-Products (NEPs) has inevitably raised the urgent question of nano-release during their synthesis, integration, processing, assembly, usage and eventually recycling or disposal at the end of their life cycle (LC). Apparently, there is a need to study and understand in a systematic manner the release mechanisms and possible exposure routes across the LC of NEPs in particular during the thermal decomposition of nanowaste. Here, we focus on the development of a novel Integrated Exposure Generation System which enables the assessment of possible environmental health and safety implications during the thermal decomposition scenario of nanocomposite materials. A specific target is the employment of the developed exposure platform for a variety of polymer nanocomposites that are currently in use in many industries and products such as automotive (engineering plastics for multiple components), electrical (plastics for switches, plugs), construction (insulation foams), packaging (extruded polymers, polystyrene), textile (polyamides, monofilaments). Finally, a detailed physicochemical, morphological, and toxicological characterization of by-products from the thermal

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decomposition of nanowaste will be performed utilizing the developed exposure system. The target is to link biological responses and properties of released aerosol and residual ash to specific NEP properties and thermal decomposition parameters. Through such an understanding, safer-by-design polymer NEPs can be manufactured that retain the superior properties without exhibiting adverse effects to the environment and human health.

Plenary Lecture 5

Surface affinity: Applications of a functional assay for quantifying nanoparticle transport, aggregation, transformation and biouptake in complex systems

*Mark Wiesner (Duke University)**

Abstract: Environmental transformations and exposure are key elements in determining the environmental and health effects of nanomaterials. Tools for predicting the environmental behaviour include functional assays that can be used to evaluate nanomaterial properties in complex or reference systems. Simulations show that nanoparticles introduced in a complex, albeit greatly simplified environment exhibit a wide range of behaviors depending on their affinities for each other and their concentrations. The complexity of these interactions appears to be governed by the relative affinity of nanoparticles for each other (autoaggregation) and with background particles (heteroaggregation) and other native surfaces. A functional assay for determining the affinity of nanoparticles for complex mixtures of native particles will be presented. This talk addresses the use of a functional assay for surface affinity, the methods for quantifying surface affinity, and systems where surface affinity is likely to be important in predicting nanoparticle exposure and effects.

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Session 5A Safer by design products, production and processes

Preparing Nanostructured Membranes from Benign and Naturally-occurring Reagents

*Idris Yazgan (SUNY-Binghamton)**

Nian Du (Springfield Laboratory, U.S. Customs and Border Protection)

Omowunmi Sadik (SUNY-Binghamton)

Abstract: The integration of biological building blocks with synthetic nanomaterials may permit unprecedented ability to detect, disinfect and completely remove pathogens in water. Where by described the synthesis of biodegradable, interpenetrating polymeric networks of poly(amic) acid (PAA), glutaraldehyde-derivatized PAA (PAA-GA) and chitosan-modified poly(amic) acid (PAA-CS) using phase-inversion procedures. The characterization data from NMR, FT-IR, SEM and cyclic voltammetry confirmed the successful formation of electroactive, bifunctional, glutaraldehyde-linked PAA membranes. Toxicological, electrochemical and mechanical characterization data showed the successful formation of non-toxic, biodegradable, porous, free-standing and mechanically strong membranes. PAA-GA showed the highest modulus of 568.1 MPa followed by PAA-CS-GA (495.0 MPa). The optimized membranes were tested against three of the most common drinking water contaminants, namely *Escherichia coli*, *Citrobacter freundii* and *Staphylococcus epidermidis* with 100% removal achieved using dead-end filtration and tangential flow filtration.

Session 5A Safer by design products, production and processes

NANoREG's Safe-by-Design Concept

*Karl Hoehener (TEMAS)**

Christian Micheletti (TEMAS)^p

Cornelle Noorlander (RIVM)

Adriënne Sips (RIVM)

Abstract: The NANoREG Safe-by-Design concept is a nano-related add-on, focusing on the safety part, for existing industrial innovation processes such as the Stage Gate Model encompassing different activities and approaches.

The NANoREG Safe-by-Design concept is not a stand-alone process. The modular character allows a seamless integration into the various stages of the innovation process of enterprises developing manufactured nanomaterials (MNM), nano-enabled products and related processes.

The NANoREG Safe-by-Design concept allows the timely identification of uncertainties and potential risks as well as actively adapt an innovation or the development in order to reduce or eliminate these uncertainties and if possible the respective risks at the earliest possible stage of the innovation process. The benefits of NANoREG's Safe-by-Design concept are diverse, and composed of:

- a) Reduction of uncertainties about human and environmental health safety;
- b) Early and easier risk identification;
- c) Projects with unacceptable risks can be timely recycled or terminated;
- d) Risk reduction;
- e) Less "surprises" (i.e. unforeseen events) during the development process and market introduction;

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Session 5A Safer by design products, production and processes

Research in Sustainable Synthesis of Nanomaterials: An overview

Barbara Karn (SNO/ George Washington University)

Abstract: The basis of nanotechnology is the manufacture, characterization and use of new nanomaterials with properties that replace, improve, or create useful products. However, in order to be sustainable, these new materials must be made in sustainable ways—without generating the old pollutants, without using more energy, and without causing environmental impacts at any of their life stages.

Research into the sustainable synthesis of nanomaterials is a beginning step into making the whole enterprise sustainable. Less polluting means of synthesis such as using non-toxic solvents (e.g., supercritical CO₂, water), self-assembly, microwave technologies, photochemical syntheses, renewable starting materials, molten salts/ionic liquids, etc. are several ways in which nanomaterials can be made in a more sustainable manner. This talk will track and discuss research in sustainable synthesis of nanomaterials and barriers to its use.

Session 5A Safer by design products, production and processes

Safer by molecular design applied to industrial case studies

Anna Luisa Costa (ISTEC-CNR)

Abstract: Exposure and Hazard Features in relation to Process and NMs Physico-Chemical Characteristics and the Control of Costs, that may increase without an advantage in competitiveness. The components of “Nano design” framework towards the design of a new generation of “safe” engineered nanomaterials, will be introduced and some examples of integration of such principles within realistic nano-manufacturing exposure scenarios will be discussed. Some results, from FP7 Sanowork and Sun projects, addressing such issues are described.

Session 5B Tracking NM in complex matrices

Detection of engineered cerium oxide nanoparticles in soil

*Frank von der Kammer (University of Vienna)**

Antonia Praetorius (University of Vienna)

Thilo Hofmann (University of Vienna)

Abstract: The detection of engineered CeO₂-NPs in complex natural media is very challenging due to the low expected CeO₂-NP concentrations and the comparatively high background of Ce-containing minerals of similar size range. We here present a new analytical method, based on single particle (sp) ICP-MS analysis for identification and quantification of engineered cerium oxide nanoparticles (CeO₂-NPs). We expect pulse signals of natural Ce-containing particles to be low and to not represent the true size of the particles detected by the sp-ICP-MS. In contrast, engineered CeO₂-NPs will appear as a spike which is significantly higher than the background signal and can be used to determine the mass and number concentration as well as the particle size of the CeO₂-NPs. Our hypothesis was tested with a set of experiments using CeO₂-NP-spiked natural colloid suspensions as well as colloidal extracts of a natural soil spiked with CeO₂-NPs. With our current single-isotope method in sp-ICP-MS we are able to detect the addition of the two-fold Ce-concentration compared to the background concentration in all types of samples. Multiple isotope techniques are currently investigated to extend our method by enabling the use of elemental ratios on single particle level and improving the detection limits considerably.

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Session 5B Tracking NM in complex matrices

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Session 5B Tracking NM in complex matrices

Plasmonic imaging of single nanoparticles: project NANODETECTOR

Vladimir Mirsky (Brandenburg University of Technology Cottbus-Senftenberg)

Abstract: A new technology developed within FP7 project “NANODETECTOR” provides a real-time detection of interaction of single nanoparticles with plasmonic surface. A number of the nanoparticle – surface binding events per time unit characterizes volume concentration of nanoparticles. A large value of the resonant surface allows us to detect many hundreds interactions in each frame, this leads to a very high dynamic range of nanoparticles counting and correspondingly to a high dynamic range in the concentration scale. The technology can be applied in liquid or in gaseous phases. Depending on the type of nanoparticles and experimental conditions, the detection limit for aqueous samples can be from 10 till 1000 nanoparticles per microliter. Characteristic SPR images of nanoparticles allows us to study heterogeneity of nanoparticles and can be probably used as a finger prints for identification of different types of nanomaterials. Chemical modification of the plasmonic surface as well as changes of pH or ionic strength influence on the interaction of nanoparticles with surface and can be used as additional parameters to evaluate this interaction and to distinguish between different types of nanoparticles.

Session 5B Tracking NM in complex matrices

Sensors and Nanotrackers in Complex matrices

*Omowunmi Sadik (SUNY-Binghamton)**

Victor Kariuki (SUNY-Binghamton)

Andrew Lake (SUNY-Binghamton)

Abstract: Nanotechnology is creating new discoveries in areas such as medicine, automotive, energy, agriculture, remediation, consumer products and the entertainment industry. Central to the core of sustainable nanotechnology is the need to develop characterization parameters, metrological tools and protocols that can provide information on the interactions of engineered nanomaterials with complex matrices. In this presentation, I will discuss conventional and emerging techniques that are available for

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characterizing engineered nanoparticles in complex matrices. I will also review the need to develop new instruments and/or further refinement of existing tools. Examples include microscopy (TEM, SEM, HRTEM, DLS, SNOM), chromatography (HDC, FFF), mass spectroscopy (ICP-MS, SEC-ICP/MS, MALDI, FFF-ICP-MS), sp-ICP-MS and electrochemical techniques. Case studies will be presented from the authors' laboratories for the design of a portable nanoparticle analyzer based on tangential flow filtration and electrochemical detection (EC-TFF). The development of personal monitors for nanoparticles that are equipped with poly (amic) acid membrane filter electrodes (PMFE) arrays to track, capture, isolate, and detect engineered nanoparticles will be discussed. Finally, I will present current research in our laboratory focusing on novel sensors for nanostructured silver, Fe₂O₃, fullerenes, TiO₂ and ceria.

Session 5B Tracking NM in complex matrices

Tracing and Quantitative Measurements of Inorganic Nanoparticles Amounts in Biological Tissues by Nuclear-Physical Methods

Anna A. Antsiferova (Moscow Institute of Physics and Technology)

Vyacheslav A. Demin (Moscow Institute of Physics and Technology)

Yurii P. Buzulukov (Moscow Institute of Physics and Technology)

Vladimir F. Demin (Moscow Institute of Physics and Technology)

Pavel K. Kashkarov (Moscow Institute of Physics and Technology)

Abstract: The problem of nanosafety appeared about 10 years ago and is due to wide use of nanoparticles (NPs) in different areas of industry. It includes a row of important questions such as determination of NP biokinetics in organism, its toxicity and so on. In order to answer these questions NPs content must be analyzed in complex biological media. One of the best way for this purpose is an application of nuclear-physical methods which demonstrate ultimately high integrity, precision and ability to measure quantitative amounts of NPs of bioessential elements in biological tissues. Neutron Activation Analysis (NAA) and Radioactive Labeling technique were developed for study of biokinetics of some widely used NPs such as silver, gold and titanium dioxide NPs. Each kind of NPs requires its unique approach in this way. For example, silver and gold provide isotopes with quite satisfactory characteristics in the process of neutron activation but titanium dioxide doesn't. The approach of detecting of titanium dioxide NPs was found in radioactive labeling of these NPs by fast protons. With the application of NAA some important results were obtained. E.g., gold NPs were mostly accumulated in rat kidneys, while silver NPs were found in large amount in liver and brain. It was demonstrated that silver NPs easily penetrate through blood-brain barrier. Moreover, rather low level of excretion of silver NPs from brain was shown that can be of great practical value. The work was financially supported by Ministry of Education and Science of the Russian Federation (grant № RFMEFI57514X0072).

Session 5B Tracking NM in complex matrices

The meaning of Characterization, and Biological Identity

Ken Dawson (University College Dublin)

Abstract: We discuss the meaning of biological identity of nanoparticles, making effort to stress the role of the whole system (exposure conditions etc) in that identity. Some new results are announced that suggest the role of more molecular thinking in this arena may be feasible.

Session 5B Tracking NM in complex matrices

European standardization project on detection and identification of nano-objects in complex matrices

*Michael Stintz (TU Dresden)**

Daniel Göhler (TU Dresden)

Abstract: The coating industry processes numerous materials within their products, which are covered by the definition of nanomaterials according to ISO/TS 80004-1:2010. There are several potential release scenarios for nano-objects studied during processing and use of coating products in a national German project, covering powder, suspension and composite state. In order to characterize particulate emissions during spray-can and spray-gun application, a simple spray channel was developed. To ensure occupational and instrumental safety, the spray channel was implemented in a special designed experimental setup. The spray-aerosol characterisation was performed according to the systematic approach, i.e. among others macroscopic spray process characteristics were analysed in addition to the particulate release. An Engine Exhaust Particle Sizer, an Aerodynamic Particle Sizer and a Condensation Particle Counter were operated for the determination of number-weighted particle size distributions and particle number concentrations from a few nanometres up to several micrometres. Particle nature analyses were performed on electrostatically precipitated spray aerosol particles by means of scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray spectroscopy. Release data will be given for four types of coatings doped with three types of nanoparticle additives that were aerosolized by two kinds of spray cans a manual gravity spray gun.

Session 5C Life cycle thinking & LCA

Sustainable Nanoproducts through Life Cycle Thinking and Life-Cycle Assessment

*Michael Steinfeldt (Universität Bremen)**

Henning Wigger (Universität Bremen)

Abstract: Nanotechnology is frequently described as an enabling technology and fundamental innovation, i.e. it is expected to lead to numerous innovative developments in the most diverse fields of technology and areas of application in society and the marketplace with sustainable and environmental benefits. As a result and to enable sustainable nanoproducts in a life cycle perspective, the following questions arise: What is the environmental impact of the production of nanomaterials? What is the influence of these nanomaterials on the environmental impact of new (prospective) applications? Which kind of nanoapplications we need in future to realize high environmental (sustainable) benefits?

This contribution tries the answer of the questions in three steps: i) By giving an overview of existing studies of published life-cycle assessments (LCAs) of the manufacture of nanoparticles and nanocomponents; ii) It analyzes the results of existing and expected nanotechnology-based applications also giving a current overview for the quantification of environmental relief potentials of this developing technology lines and discuss the iii) characteristics of nanoapplications with high environmental (sustainable) benefits. The focus is placed on the potential environmental (sustainable) relief provided by nanotechnology-based applications. Risk aspects, particularly in dealing with nanomaterials are brought up for discussion however it is not the focus of this contribution.

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Session 5C Life cycle thinking & LCA

Nanomaterials release from product's life cycle: the GUIDEnano project

*Alejandro Vilchez (LEITAT Technological Center)**

David González-Gálvez (LEITAT Technological Center)

Delphine Boutry (CEA)

Stefano Zuin (Venice Research Consortium)

Socorro Vázquez-Campos (LEITAT Technological Center)

Abstract: Currently the potential impacts of engineered nanomaterials (ENMs) on humans and the environment have generated considerable research interest, since their use and diversity of applications in commercial products have grown extensively over the past decade, and it is expected to continue growing. The main objective of this work is to develop a strategy to identify and predict amount of release of ENM and the form these released ENMs (e.g. free, aggregates, embedded in matrix and/or ion leaching, as added or degraded) throughout the life cycle of nano-enabled products, within the framework of the GUIDEnano FP7 European research project. This project ultimately aims at developing innovative methodologies to evaluate and manage human and environmental health risks of nano-enabled products, considering their whole life cycle. Results obtained from literature review will be presented, categorized by type of product tested, experimental set-up, receptor compartment or released material properties. Special attention has been paid to both use and end-of-life life cycle stages of the nano-enabled products. In addition, a series of experimental simulations based on the industrial case studies proposed within GUIDEnano project will be described. The presentation will also outline the main findings up to 12 months of the ongoing project.

Session 5C Life cycle thinking & LCA

Probabilistic modelling of prospective environmental concentrations of Gold nanoparticles from medical applications as a basis for risk assessment

*Indrani Mahapatra (University of Birmingham)**

Tianyin Sun (EMPA)

Jamie R Lead (University of South Carolina)

Abstract: Unique physical and chemical properties and ease of surface functionalisation of GNPs makes it attractive for widespread use in the medical field. GNPs can be used as imaging agents, targeted delivery of therapeutic agents, photodynamic and photothermal therapy, detection of biomarkers, immunoassays, antibacterial, etc. However, mass production and use might give rise to potentially new environmental hazards and risks in the future, as it has been found that GNPs may have toxic effects. In this study, we (1) estimated the total consumption of GNPs used in medical applications for the UK and USA; (2) modelled the prospective GNPs flows along the product life cycles using established probabilistic material flow modelling approaches and predicted the environmental concentrations (Gottschalk et al. 2009); and (3) conducted an environment risk assessment (ERA) for aquatic and terrestrial compartments by comparing the prospective environmental concentrations with probabilistic species sensitivity distribution. Highest concentrations of GNPs were found in the sludge from Sewage Treatment Plants, for both countries, reaching 100 $\mu\text{g/kg}$. Results from the ERA for terrestrial and aquatic environments indicate that there is currently no risk from GNPs, although the scarcity of data at present means that the model should be re-run as data emerges.

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Session 5C Life cycle thinking & LCA

Silver nanoparticles biokinetics study by mathematical modelling of their transport in living organism

*Vyacheslav A. Demin (Moscow Institute of Physics and Technology)**

Ivan V. Gmoshinsky (RAS Scientific Research Institute of Nutrition)

Vladimir F. Demin (Moscow Institute of Physics and Technology)

Anna A. Antsiferova (Moscow Institute of Physics and Technology)

Pavel K. Kashkarov (Moscow Institute of Physics and Technology)

Abstract: In this work we demonstrate the possibilities of mathematical "chamber" model of inorganic nanoparticles (NPs) transport (absorption, distribution and bioaccumulation) in living organism, on an example of silver NPs in laboratory rats. When constructing a model, data of experimental work were used about the bioaccumulation and biodistribution of silver NPs with average diameter of 35 ± 15 nm, radiolabeled by ^{110}mAg . In a minimally acceptable form model included all "chambers" in which the content of the NPs throughout the duration of the experiment was not lower than 20-25 % of the content in the blood, namely the gastrointestinal tract (GIT), blood itself, bone-muscular carcass, liver and spleen. Transport of NPs within these «cameras» was described by a system of 5 independent linear differential equations of the 1st order. Solution of this system in numerical form, taking into account a timing of the excretion of NPs from the GIT with the feces, made it possible to determine the rate constants of inter-organ NPs transfer. Using them the calculation was done of the peak (maximum) and quasi-stationary NPs content in critical organs targets, respectively for the cases of acute (single) and subchronic (repeated) administration into the GIT, depending on the dose of NPs. The results obtained indicate the prospects of the method of mathematical modeling for inter-organ transport and distribution of NPs to assess their possible toxic effects on the system level, using previously obtained in vitro results and biokinetic studies. The work was financially supported by Ministry of Education and Science of the Russian Federation (grant № RFMEFI57514X0072).

Plenary Lecture 6

Entropic control, Sustainable Nanotechnology at the molecular level

John Warner (Warner Babcock Institute for Green Chemistry, LLC)

Abstract: TBA

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Session 6AToxicology and human health risks

Distribution and Biological Effects of Fullerene C60, Titanium Dioxide and Silver Nanoparticles after Single and Multiple Intragastrical Administrations to Rats

*Olga D. Hendrickson (Russian Academy of Sciences)**

Anatoly V. Zherdev (Russian Academy of Sciences)

Boris B. Dzantiev (Russian Academy of Sciences)

Olga V. Morozova (Russian Academy of Sciences)

Svetlana M. Pridvorova (Russian Academy of Sciences)

Tatyana A. Platonova (Russian Academy of Sciences)

Alexander I. Yaropolov (Russian Academy of Sciences)

Sergey G. Klochkov (Russian Academy of Sciences)

Sergey O. Bachurin (Russian Academy of Sciences)

Abstract: Investigations of the biological effects of nanomaterials, their biodistribution in target organs and tissues after different dosage and routes of exposure are important for assessing the risk of nanotechnology products. The present work is an in-depth study, including the investigation of the localization of fullerene C60, titanium dioxide and silver nanoparticles (NPs) after intragastrical exposure of rats under conditions of acute (single administration) and sub-acute (multiple administrations) toxicity, the observation of the status of experimental animals, pathomorphological analysis of their internal organs, and measurement of the dynamics of key hematological and biochemical parameters. NPs localization in organs of the exposed rats was revealed by mean of different analytical techniques: atomic absorption spectroscopy, transmission electron microscopy, and HPLC with spectrophotometric detection. It was shown that singly or multiply administered NPs absorbed from gastrointestinal tract with infiltration into the bloodstream and translocation into secondary organs. Some biochemical parameters and hematological indices of the treated rats changed in comparison to control animals. However, the exposure did not cause lethality, substantial behavior deviations, water and food consumption, pathomorphology of the internal organs. The amounts of NPs accumulated in organs and tissues are far smaller than the administered dose that is the indication of their efficient excretion. This study was funded by MARINA project (contract № 236215) of the EU 7th Framework Program.

Session 6AToxicology and human health risks

Role of Biological Monitoring in Nano-Safety

*Enrico Bergamaschi (University of Parma)**

Irina Guseva Canu (French Institute for Public Health Surveillance)

Craig A. Poland (Institute of Occupational Medicine, UK)

Adriele Prina-Mello (Trinity Centre of Health Sciences, Dublin, Ireland)

Abstract: The ability to predict and then mitigate potential health effects is mandatory for sustainability of nanotechnology. Although screening strategies to expedite hazard and risk assessment (RA) of engineered nanomaterials (ENM) proceed, the complex and multi-faceted nature of events occurring at the nano-bio interfaces at the organism level means that currently the full replacement of in vivo assessment is not possible. Since the chemical and biological identities of ENM are subject to changes in environmental settings from emission sources to site of accumulation and effect within the body, a case-by-case approach to assess their hazard potential using simplified models to predict complex outcomes is required. It is therefore foreseeable that the knowledge-based body of experimental data can

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take advantage from a complementary approach relying on biomarkers of exposure to detect relevant effects in target organs at early and reversible stages and to identify subgroups at risk. Though the issue of (nano)specificity of biomarkers is challenging, yet evidence resulting from experimental and epidemiological studies with conventional particles suggests similar paradigms for particle/nanoparticle hazard. Validation of biomarkers in human studies will allow to overcome uncertainties due to the use of simplified models, lack of quantitative data, and provide RA with relevant information.

Session 6A Toxicology and human health risks

Synergistic TLR4-dependent effects of titanium dioxide nanoparticles and LPS on the activation of murine macrophages

*Massimiliano Bianchi (University of Parma)**

Manfredi Allegri (University of Parma)

Ovidio Bussolati (University of Parma)

Enrico Bergamaschi (University of Parma)

Abstract: Nanomaterials may bind bioactive environmental contaminants, such as bacterial endotoxins, thus potentially acting as carriers for toxicants. To investigate the functional implications of this interaction, we have investigated the inflammogenic response mediated by two preparations of TiO₂ nanoparticles (NP), co-administered with lipopolysaccharide (LPS), in Raw264.7 murine macrophages. TiO₂ NP synergized the effect of LPS on both Nos2 mRNA and Nos2 protein expression as well as on NO production. TiO₂ NP also potentiated the LPS effects on Ptgs2 expression and cytokine secretion. NP uptake was reduced by the cytoskeletal drug cytochalasin B thus suppressing the synergy between TiO₂ NP and LPS. Pre-treatment with the TLR4 inhibitors polymyxin B and CLI-095 abolished the synergistic effect that was also partially hampered by the inhibition of p38 but not of ERK1/2, MAPK. This findings suggest that TiO₂ NP enhance macrophage activation by LPS via a TLR4-dependent mechanism that involves p38 and an intracellular site; other NP, such as polystyrene NP, show the same effects. Different NP may deliver bioactive molecules to target organs through a “Trojan Horse effect”, thus enhancing macrophage activation leading to increased inflammation and worsening inflammatory status. Supported by EU FP7 Project Sanowork (Grant NMP4-SL-2012-280716)

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Session 6AToxicology and human health risks

Feasibility of using in vitro toxicity studies for human risk assesment of nanomaterials

*Joan Cabellos (LEITAT Technological Center)**

Gemma Janer (LEITAT Technological Center)

Socorro Vezquez-Campos (LEITAT Technological Center)

Craig A. Poland (Institute of Occupational Medicine, UK)

Enrico Bergamaschi (University of Parma)

Lucia Migliore (University of Pisa)

Anna Luisa Costa (ISTEC-CNR)

Abstract: Given ethical, technical and economical considerations, the use of in vitro testing of nanomaterials is considered a preferred alternative to in vivo testing. However, the use of in vitro testing for human health risk assessment is still challenging. The hazard data generated within the Sanowork project is based on a battery of in vitro studies. The nanomaterials included in the project have several safer by design modifications. In an attempt to use as much as possible in vitro data on the risk assessment, we developed a theoretical approach to extrapolate provisional worker exposure limits on the basis of such in vitro studies. This approach was mainly based on the hypothesis that comparing the in vitro toxicity profile of the Sanowork nanomaterials and Benchmark nanomaterials together with in silico dosimetry modelling, would allow calculating approximated human reference values. Benchmark nanomaterials were selected so that they share relevant toxic mechanisms of action, and human reference values or in vivo relevant data are available. Prior to applying the Sanowork Approach, a proof of concept of the whole process was performed using a group of TiO₂ nanomaterials for which we were able to obtain both in vitro and in vivo data from the literature.

Session 6AToxicology and human health risks

The relationship between the biological effects of Titanium Dioxide nanofibers and their aspect ratio

*Manfredi Allegri (University of Parma)**

Enrico Bergamaschi (University of Parma)

Massimiliano Bianchi (University of Parma)

Abstract: A strict relationship between the toxicity of fiber-like nanomaterials and their aspect ratio emerges from the fiber paradigm. As a consequence, fiber shortening is expected to reduce material toxicity. Titanium dioxide nanofibers (TiO₂NF) are a novel fibrous nanomaterial, used in several industrial applications but still requiring complete toxicological characterization. We evaluated the toxicity of commercial TiO₂NF (length, 0.2-30µm; thickness, 0.2 to 0.6µm; aspect ratio 1:28, consisting of primary TiO₂ nanoparticles), before and after ball-milling, which lowered their aspect ratio to 1:8. The evaluated endpoints were cell viability, inflammatory markers, and trans-epithelial electrical resistance (TEER), an indicator of the epithelial barrier competence. TiO₂ NF exhibited cell specific cytotoxicity, markedly decreasing viability in A549 epithelial cells but not in Raw 264.7 macrophages. A dose- and time-dependent TEER decrease in CaLu-3 cell monolayers was also detected. Ball-milling significantly mitigated these effects but, conversely, enhanced the expression of inflammatory markers in macrophages. This study indicates that TiO₂NF exert significant toxic effects including cytotoxicity, macrophage activation and epithelial barrier impairment. While aspect ratio reduction mitigates TiO₂NF effects on cell viability and epithelial barriers, it enhances the inflammogenic activity of the nanomaterial, indicating that different structural determinants are implied in the biological effects of fiber-like nanomaterials.

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Session 6B Occupational and consumer exposure

Comparing workers measured dust exposure with predicted exposures using a NF/FF model, NanoSafer, and the ART exposure assessment tools

*Antti J. Koivisto (National Research Centre for the Working Environment)**

Ismo K. Koponen (National Research Centre for the Working Environment)

Alexander C.Ø. Jensen (National Research Centre for the Working Environment)

Kirsten I Kling (National Research Centre for the Working Environment)

Marcus Levin (National Research Centre for the Working Environment)

Keld A. Jensen (National Research Centre for the Working Environment)

Abstract: Here we measured near field (NF) and far field (FF) concentrations in a paint factory during pouring of paint pigments/fillers from 25 kg and 500 kg bags [1]. The pigments/fillers dustiness indices were characterized by using the down-scaled EN15051 dustiness drum [2]. Dustiness indices were used to calculate the dusts emission rates used in the tools by taking into account modifying factors [3]. The measured concentrations were compared with concentrations predicted with a NF/FF model (e.g. [4]), the ART, and the NanoSafer. We found that a handling energy value deviated significantly from previously assigned values. We found that the ART tool overestimates ~5 times the exposure concentration and the emission rate is not directly related to the amount of material used. Studies in progress on the comparability of the basic exposure estimations in the different tools will be presented. As expected, the emissions and modifying factors need to be studied in well controlled environments to improve our understanding.

Session 6B Occupational and consumer exposure

Ranges in respirable and inhalable dustiness and dustiness kinetics of nanomaterial powders as determined with the prototype small rotating drum – priority parameters for exposure assessment

*Keld Astrup Jensen (National Research Centre for the Working Environment)**

M Levin (Technical University of Denmark)

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A.Ø. Jensen (National Research Centre for the Working Environment)

B. Liguori (Technical University of Denmark)

Antti J. Koivisto (National Research Centre for the Working Environment)

Ismo K. Koponen (National Research Centre for the Working Environment)

Abstract: The OECD WPMNM (Working Party on Manufactured Nanomaterials) has listed dustiness as a priority data for risk assessment of nanomaterials. To enable testing of small volumes and improve handling safety, Schneider and Jensen developed a miniaturized version of the EN15051 rotating drum for nanomaterial testing. This small rotating drum (SRD) is now under standardization in CEN. Here, the results obtained on more than 80 different powders tested using the SRD are discussed in regard to the traditional mass-based respirable and inhalable dustiness indices, their size-characteristics, and dustiness kinetics. These are parameters deemed important for use of dustiness results in exposure assessment modeling under development in e.g., the EU FP7 project SUN. The results demonstrate an extreme range in dustiness levels and variations in dustiness kinetics from instant release to almost constant rate “emitters”. Recently, these two parameters were used product evaluation of pharmaceutical powder ingredients. The observed dustiness characteristics indicates that grouping powders by dustiness indices is a difficult task and that the conventional dustiness categories established in EN15051 may need reconsideration.

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Session 6B Occupational and consumer exposure

Nanoparticle Surface Activity: Understanding, Measuring and Integrating it into Inhalation Dosimetry

*Dhimiter Bello (UMass Lowell)**

Pongsit Boonruksa (UMass Lowell)

JInde Zhang (UMass Lowell)

Jacqueline Isaacs (Northeastern University)

Susan Woskie (UMass Lowell)

JInde Zhang (UMass Lowell)

Joey Mead (UMass Lowell)

Abstract: This study investigated airborne nanoparticle exposures generated during injection molding and grinding of polycarbonate carbon nanotube composites (PC/CNT). Particle number concentration and size distribution were measured using a suite of real time instruments. Area samples were collected using an electrostatic precipitator and examined by transmission electron microscopy for particle morphology. Breathing zone samples were collected on nucleopore filters. Respirable fibers were counted with a scanning electron microscope. The results showed that processing and grinding during recycling of PC/CNT released airborne nanoparticles with a geometric mean (GM) particle concentration from 4.71×10^3 to 1.75×10^6 particles/cm³. The ratios of GM particle concentration measured during the process to the background particle count were high up to 1.3 (loading), 1.9 (melting), and 1.4 (molding), and 101 (grinding), indicating significant nanoparticle emissions from these processes. The various particle morphologies were observed including respirable and nanoscale particles, particles with protruding CNTs, and fibers, but no free CNTs. The breathing zone respirable fiber concentration during grinding ranged from non-detectable to 0.13 fiber/cm³. No clear evidence that nanoparticle exposures were affected by the number of recycling cycles (up to 20). Exposures controls should be instituted during synthesis, processing and recycling of PC/CNT composites.

Session 6B Occupational and consumer exposure

Assessment of dermal exposure to nano-objects, and their agglomerates and aggregates (NOAA); Results from a pre-normative research project

*Derk Brouwer (TNO Innovation for Life)**

Francesca Larese-Filon (University of Trieste)

Martin Roff (Health & Safety Laboratory)

Abstract: Occupational dermal exposure to NOAA can be relevant in view of penetration through the skin, local skin effects and inadvertent ingestion. The potential for consequences of dermal exposure to nanomaterials will be determined by both parameters of exposure and other parameters. With respect to penetration and local effects, the integrity of the skin is an important determinant, whereas for ingestion the frequency of hand-mouth will affect the oral intake.

Size is an important factor for penetration of the nanoparticle through the skin. It has been demonstrated that only very small particles (< 4nm) can penetrate the intact skin, whereas larger particles can only penetrate and permeate in damaged skin. Since the condition of the skin is important, the combination of job titles with high incidence of skin disruption and the use of NOAA or nano-enabled products indicates potential risk for enhanced skin penetration or local effects.

Explorative research showed that the most promising method to measure exposure on skin in view seems to be the removal from (surrogate) skin, by tape lifting, and consecutive analysis by SEM.

All results were connected into a framework that will be helpful to flag potential risk due to exposure to NOAA.

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Session 6B Occupational and consumer exposure

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Session 6C Environmental exposure, release & fate

Single particle ICPMS based methods for tracking environmental leaching of nanoparticles from consumer products

*Frank von der Kammer (University of Vienna)**

Jana Navratilova (University of Vienna)

Thilo Hofmann (University of Vienna)

Abstract: Globally industrial production of engineered nanoparticles increases dramatically, what raises concerns about their release and fate in the environment. There are numbers of methods for nanoparticle characterization and detection including TEM, DLS, NTA and many others but not one of these methods is fit for purpose regarding mainly low detection limits in ng/L range, which is environmentally relevant. During the last few years single particle ICPMS (spICPMS) technique showed a great potential for detection of gold and silver nanoparticles in the ng/L concentration levels.

Within the project SUN we are developing spICPMS method using triple quadrupole ICPMS to study potential release of metallic nanoparticles from nanoparticle based consumer products into simulated aquatic environment namely for Fe₂O₃, CuO and TiO₂ nanoparticles. In this contribution the spICPMS method is evaluated in terms of particle size detection limit for Fe, Cu and Ti based nanoparticles and spICPMS method development strategy is presented.

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Session 6C Environmental exposure, release & fate

Novel method to address the environmental impact of nanomaterials in the use phase: the SUN approach

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Abstract: It is now acknowledged that nanomaterials will experience several transformations along their life cycle, upon formulation, production processes, aging and disposal. However most efforts still focus on assessing the impact of pristine nanomaterials, while formulated and aged nanomaterials are rarely investigated, resulting in significant knowledge gap. This situation is due for a great part to the difficulty of preparing large amounts of aged materials. Indeed all published studies only report few amounts of released nanomaterials, which are insufficient for ecotoxicity testing. SUN project proposes a new approach to this issue. Based on the observation that nanomaterials are most often released within their product matrix, a cryo-milling protocol was developed to produce large quantities of fragmented products (FP) that can be aged afterwards to reproduce any transformation the material would normally experience under use. To validate this approach a case study was carried out on polyethylene with 1% Fe₂O₃ nanoparticles (Fe₂O₃_PE), serving as pigments with color index PR101 that achieves the longterm stability of pigment particles and yet is transparent in thin films due to a diameter of only 32nm. The response of Fe₂O₃_PE FP to 3 months weathering in a climatic chamber was investigated and compared to that of small plates of the same material, representative for the final product (car bumper). Release was quantified and transformations of solid matrix induced by weathering in both cases were monitored by IR spectroscopy and a combination of X-ray techniques (XRD, μ XRF, micro and nano X-ray tomography).

Session 6C Environmental exposure, release & fate

Interactive spICP-MS data treatment using Nanocount

*Geert Cornelis (Gothenburg University)**

Abstract: Interest in applying single particle ICP-MS (spICP-MS) in risk assessment of inorganic engineered nanomaterials (ENM) has been increasing because it is currently the only technique capable of measuring number-based particle size distributions of ENM at the likely low number concentrations in complex environments. However, the cumbersome treatment of large spICP-MS datasets slows the widespread adoption of spICP-MS. Nanocount[®], furthers this adoption by accepting data from any ICP-MS so that it can interactively be calculated into particle size distributions. The capabilities to correct for drift and to distinguish dissolved and nanoparticulate signals are demonstrated using non-ideal data of 15 nm Au NPs and FAST spICP-MS data of Ag ENM in wastewater treatment sludges. It is shown how more advanced data-treatment algorithms such as deconvolution are required to measure the lowest sizes possible where considerable overlap between dissolved and particulate signals exists. Moreover, the existence of many different data-treatment algorithms such as n x sigma, K-means clustering, deconvolution and FAST spICP-MS as well as different representations of the final particle size distribution can lead to widely different results. It is thus argued here that a large portion of the variability in spICP-MS results can be explained by differences in data treatment.

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Session 6C Environmental exposure, release & fate

Nanotechnology : the missing piece of the life puzzle

Gilbert M. Rios (European Membrane House (EMH))

Abstract: In all the countries the appetite of scientists for nanotechnology, and the belief in its ability to provide more efficient solutions to technical issues that are facing our societies, have been growing very fast during the last decade. Also, a tremendous development of membrane technologies has led to consider them like "dominant technologies", with the emergence of a new think-tank / action-tank named "membrane engineering" and a lot of applications with environmental issues (water, air...). Because many of these technologies depend on nano-scale processes, it is reasonable to expect a strong impact of nanotech on performance of membrane systems of the future, particularly in tremendous field such as desalination. Nature on its side has solved long ago the problem of controlling the selective transfer of water and salts, with wonderful nano-tools: aquaporins, ion conducting channels ... Today researchers are trying to imitate nature with new aquaporin-laced polymer membranes, aquaporin mimicking carbon nanotubes... In what extend human achievements for highly efficient membranes have been delayed by our ignorance of nanotech? In what extend sustainability may be affected by revolutions in progress on this area? This is the kind of questions that our presentation intends to deal with.

Session 6C Environmental exposure, release & fate

Speciation and mechanisms of nanomaterial release from nano-enabled products during their life cycle: Self-cleaning cement as building material case study

Nathan Bossa (INERIS)

Abstract: The industrial scale production and wide variety of applications of manufactured nanoparticles (NPs) and their possible release into the natural aquatic environment have produced an increasing concern among the nanotechnology and environmental science community.

Nanomaterials are used in construction to improve the properties and functions of commonly used building materials like cement, glass, paint... A part of this production concerns a new type of cement, called self-cleaning cement which maintains clean and white wall fronts. Such building materials may also provide interesting pollution-reducing properties.

The technology is based on the photocatalytic property of nano-TiO₂ added in the cement matrix. During continuous UV radiation exposure, TiO₂ NPs lead to the oxidation (i.e. degradation) of compounds adsorbed at the cement surface. Such nanomaterial application in building construction is promising as it exhibits improved properties but its environmental validation (in terms of impacts and risks associated with the incorporation of TiO₂ NPs) is also required.

Indeed cement is altered during their use when exposed to water (e.g. rain draining on cement wall). An altered layer is then formed at its surface where numerous and complex reactions occur such as cement phase congruent or incongruent dissolution, secondary phase formation, etc... This layer exhibits an increase of porosity. Cement leaching behavior and associated elements released into the environment, is well described in the literature but the behavior of the incorporated TiO₂ NPs is currently unknown. Release of TiO₂ NPs, more precisely, the emission of nano-products degradation residues (NDR) into the environment (waters, soils ...) is suspected as alteration time increases.

The aim of this study is to determine the mechanisms of nano-TiO₂ release from a self-cleaning cement during aging process and to identify cement parameters controlling it. We performed cement accelerating aging procedure on cement with various initial porosities to generate different rates of cement matrix degradation. One of the main objectives was to address the influence of cement porosity on leaching behaviour of TiO₂ NPs. To simulate the alteration phase, static leaching tests (liquid/solid ratio (L/S) of 100) were performed during 7 days. Each sample was placed within a dialysis membrane (10 kDa) filled with ultrapure water and submerged in a leachate solution (ultrapure water) to isolate the released particulate fraction from the sub-released soluble fraction. The elements released (particulate and soluble fractions) and their kinetic were quantified by ICP-OES and characterized with DLS and TEM.

We analyzed the solid phase (core to altered layer) using several X-ray based techniques: XRD (X-Ray Diffraction), μ -XRF (micro X-Ray Spectroscopy) and an unprecedented combination of nano and micro X-ray computed tomography to perform a complete altered cement matrix characterization including pore structure.

Original results concerning the low-stability of the cement matrix while NDR are released in fresh water will be detailed with regards to the size and surface properties of nano-TiO₂. More over a deep investigation of the alteration mechanisms of cement will help deciphering the cement porous network properties that control nano-TiO₂ release. Based on our results a predictive strategy will be proposed.

Poster Presentation Session

Effects of Maturation conditions on the Structure of Hydroxyapatite Nanopowder

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Aurora Mocanu (Babes-Bolyai University of Cluj-Napoca)

Abstract: Series of syntheses were made to control hydroxyapatite (HAP) crystallinity, shape of particles and their size distribution using hydrothermal technique. HAP powders were synthesized by mixing aqueous solutions of precursors at the Ca/P ratio of 1.667 characteristic for HAP formation at alkaline pH. Then, formed particles were matured for different times at various temperatures within the mother solutions. Resulted precipitates were filtered, washed carefully and finally lyophilized. Afterwards, experiments were undertaken for crystallographic analysis of nanopowders. X-ray diffraction (XRD) data provide a firm discussion in agreement with TEM and AFM images. It was found that the crystallinity and morphology of HAP particles as well as BET surface area and porosity of nanopowders are strongly dependent on maturation conditions. The general aspect of nano HAP is from needle crystals to spherical or fibrous features. Maturation conditions have produced the same powder, thus assuring the reproducibility of these materials. Definitely, various structures of obtained HAP nanopowders can have different biological significance having different bioactivity. This work forms a fundamental base for our actual investigations into the influence of various HAP structures used as scaffolds on cell cultures, which might be related to their in vivo biological significance.

Poster Presentation Session

Electrochemical CO₂ reduction for fuel production

*Jihui Choi (Chung-Ang University)**

Ho Young Kim (Chung-Ang University)

Soo-Kil Kim (Chung-Ang University)

Abstract: Electrochemical CO₂ reduction has been widely studied as one of the appropriate methods for the reduction and conversion of CO₂. Electrochemical reduction of CO₂ is a technology to convert CO₂ into fuels, such as methanol, formic acid, syngas or hydrocarbons, using electric energy. The product depends on the type of catalyst and reaction conditions, such as electrolyte, reduction potential, etc. In this study, CO was chosen for the target product, which is a component of syngas. We have investigated various types of electrochemically fabricated Ag catalysts, of which the characteristics were controlled in terms of substrates, morphologies, etc. Electrochemical CO₂ reduction was performed in aqueous solution in a home-made H-type cell separated by a proton exchange membrane. The gaseous product was directly delivered into the sampling loop of the gas chromatography system for analysis. We report that the faradaic efficiency and amounts of produced CO are related to the type of substrate and morphology. Detailed information about the effects of process variables on the efficiencies will be introduced at the meeting.

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Poster Presentation Session

Fabrication of Transition Metal Alloy Catalysts for Hydrogen Evolution via Water Electrolysis

*Ho Young Kim (Chung-Ang University)**

Jihui Choi (Chung-Ang University)

Soo-Kil Kim (Chung-Ang University)

Abstract: Water electrolysis is a promising method to produce a high purity and a large amount of hydrogen. Noble metals in hydrogen evolution reaction have the advantage of superior activities, while the cost of noble metal is still obstacle for the commercialization. To solve this problem, cheap non-noble metal catalysts have been largely investigated. However, the non-noble metals in acidic electrolyte also have low corrosion resistance as a disadvantage. This problem can be overcome by using the metal alloy catalysts.

In this study, we have investigated the alloy catalysts for hydrogen evolution reaction (HER) in the acidic electrolyte. Co-Cu alloys of various compositions were prepared by electroplating. Activity of Co-Cu alloy catalysts were measured by Cyclic Voltammetry using aqueous sulfuric acid solution. The surface morphology of Co-Cu alloy was characterized by FE-SEM and chemical composition was analyzed by EDS. Also, XRD was used to analyze the crystal structure according to the composition change of Co-Cu. Prepared Co-Cu alloy catalyst was found to exhibit high activity and stability in acidic aqueous solution. And the activity enhancement was explained in terms of the material characteristics of Co-Cu alloys.

Poster Presentation Session

Addressing the Complexity of Water Chemistry in Environmental Fate Modeling for Engineered Nanoparticles

*Nicole Sani-Kast (ETH Zurich)**

Martin Scheringer (ETH Zurich)

Konrad Hungerbühler (ETH Zurich)

Abstract: Current environmental fate models for engineered nanoparticles (ENPs) have limited applicability because they employ constant environmental conditions along the modelled system or a highly specific environmental representation. We, therefore, developed a novel modelling strategy that: 1) incorporates spatial variability in environmental conditions in an existing ENP fate model; and 2) analyzes the effect of a wide range of randomly sampled environmental conditions. Using this approach we investigated the transport of nano-TiO₂ in the Lower Rhone River (France) under numerous scenarios of environmental conditions. The predicted concentration profiles of nano-TiO₂ were then grouped according to their similarity by using cluster analysis. The analysis resulted in a small number of clusters. In each cluster, a strong association was found between the water conditions in regions close to the ENPs emission source and the cluster membership of the corresponding concentration profiles. In particular, water compositions favouring heteroaggregation between the ENPs with suspended particulate matter resulted in clusters of low variability. These conditions are, therefore, reliable predictors of the eventual fate of the modelled ENPs. Our results, therefore, shift the focus of future modelling and experimental research of ENP environmental fate to the water characteristic in regions near the expected ENP emission sources.

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Poster Presentation Session

Benchmark dose (BMD) analysis of CuO and WCCo nanomaterials cytotoxicity in hepatocyte and macrophage cell lines

*Daniele Pantano (Heriot Watt University)**

Lucian Farcal (Karolinska Institutet)

Abstract: This study, performed within the frame of FP7-SUN (Sustainable Nanotechnologies), aimed to evaluate the effects of nanomaterials (NMs) in two different cellular models, hepatocytes and macrophages. The NMs selected for this study were the pristine forms of copper oxide (CuO) and tungsten carbide with cobalt binder (WCCo). Additionally the cells were exposed to CuCl₂, CuSO₄ and CoCl₂ as controls. The cytotoxicity and the inflammatory potency of NMs after 24h of exposure were investigated in the C3A hepatocellular carcinoma and RAW264.7 macrophage cell lines. The cell viability was measured using the Alamar Blue (resazurin) assay and the results were used for benchmark dose (BMD) analysis by R software with PROAST 38.9 package. The BMD20 and EC50 parameters were used to compare the results between the cell lines and the NMs. The results in C3A cells showed that CuO NMs (BMD20=25.80 Åµg/ml and EC50=32.54 Åµg/ml) were more toxic than WCCo NMs (BMD20=157 Åµg/ml and EC50>200 Åµg/ml). Also in RAW264.7 cells, CuO NMs showed a higher toxicity (BMD20=25.50 Åµg/ml; EC50=40.97 Åµg/ml) compared to WCCo NMs (BMD20=48.10 Åµg/ml; EC50=98.08 Åµg/ml). The cytokines (IL-1Î², IL-6, IL-8, TNF-Î± and RANTES) produced by the hepatocytes after 24 hours of exposure at several concentrations were investigated using the Luminex Assay. Similarly a set of cytokines and chemokines (TNF-Î±, IL-6, IL-1Î², IL-10, IL-12, MCP-1, MIP-1Î±, MIP-1Î², RANTES and KC) produced by macrophages were measured after 24h of exposure to different concentrations of NMs.

Poster Presentation Session

Transformation and distribution processes governing the fate and behaviour of nanomaterials in the environment: an overview

*Steffen F. Hansen (DTU)**

Nanna B. Hartmann (DTU)

Anders Baun (DTU)

Abstract: Analytical methods are currently challenged when it comes to detecting and quantifying nanomaterials in the environment. This leaves a gap between the present scientific state-of-the-art and the increasing demand for reliable measured or predicted environmental concentrations for environmental risk assessment. Chemical fate modelling is one approach to fill this gap within a short time frame. To ensure the reliability of predicted environmental concentrations informed choices are needed during model formulation and development. A major knowledge gap, hampering the further development of such model-based approaches, relates to the interplay between the nanomaterial physico-chemical properties, surrounding media/matrix composition and the underlying processes that determine particle behaviour. Here we identify and summarize key processes governing the fate and behaviour of nanomaterials in the environment. This is done through a critical review of the present state-of-knowledge. We describe the (photo)chemical, physical or biologically mediated transformation of manufactured nanomaterials due to degradation, aggregation, agglomeration, or through association with dissolved, colloidal or particulate matter present in the environment. Specific nanomaterials are used as case studies to illustrate these processes.

Key environmental processes are identified and ranked and key knowledge gaps are identified, feeding into the longer-term goal of improving the existing models for predicted environmental concentrations.

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Poster Presentation Session

Low detection limits of fluorescent nanoparticles in aquatic environments

Alberto Clemente (Instituto de Nanociencia de Aragon (INA))

M. Pilar Lobera (Instituto de Nanociencia de Aragon (INA))

Jesus Santamaria (Instituto de Nanociencia de Aragon (INA))

Abstract: Our environment is crowded with nanoparticles, some resulting from natural processes (e.g. SiO₂), and some man-made (e.g. carbon from combustion engines), the adequate tagging of ENPs is crucial to be able to (1) follow their fate in several media as well as (2) to open new challenges and opportunities in assessment, monitoring and imaging of those nanomaterials for safety and toxicological studies. Methods for efficient identification of nanoparticles in different environments are currently under research. Indeed, optical labeling of nanoparticles is also investigated for enhancing sensitivity of identification.

Our approach is based in introducing fluorescent markers such as fluorescein isothiocyanate, FITC, and ruthenium(II)-tris(1,10-phenanthroline), [Ru(phen)₃]²⁺. These fluorophores are trapped in core-shell SiO₂ nanostructures. The strong interaction between the fluorophore and the silica structure enhances the stability of the signal through time. In addition, protective silica shell prevents diverse quenching effects (solvent, pH, O₂ concentration, etc.). The analysis of TEM images have reported a FITC@SiO₂ nanoparticles of 65,3Å±3,7 nm mean diameter and a Ru(phen)₃@SiO₂ nanoparticles of 65,3Å±3,7 nm mean diameter. The performance of those labeled-SiO₂NPs as tracers was studied in several media using fluorescence spectroscopy (FS), and the corresponding detection thresholds were established. Different aqueous media were considered (miliQ water, miliQ water, drinking water, natural water) and also their behavior in a biological media (DMEM) was analyzed. FITC: Concentrations down to 15 ng/mL of FITC@SiO₂-NPs 10 ng/mL of Ru(phen)₃@SiO₂-NPs have been detected in miliQ-water, whereas concentrations up to 1000 ng/mL of FITC@SiO₂-NPs and 1000 ng/mL of Ru(phen)₃@SiO₂-NPs are necessities to be detected when natural water media was considered. In both cases, the identification of those labeled-SiO₂NPs are performed using fluorescence spectroscopy (FS) at different excitation wavelengths depending on the composition and structure of nanoparticles. Moreover, XPS and XRF analysis were performed.

Poster Presentation Session

Analyzing the emission of engineered nanoparticles in accidental sites: Development of a self-cleaning dispersion chamber for exposure assessment

Francisco Balas (Instituto de Nanociencia de Aragon (INA))

Alberto Clemente (Instituto de Nanociencia de Aragon (INA))

Jesus Santamaria (Instituto de Nanociencia de Aragon (INA))

Abstract: The release of hazardous nanoparticulate matter in accidental situations was simulated in a specially designed 13-m³ stainless steel airtight chamber, which allowed the dispersion analysis of airborne matter in a practically particle-free environment (less than 2 #/cm³) and in presence of background atmospheric aerosols. A fast recovering of the initial situation was achieved by means of a tandem HEPA-filtered air and deionized water system. Both unintended spilling of silica-based nanoparticulate powders and continuous emission of 100-nm SiO₂ nanoparticles were used as aerosol generation events. The emission of airborne nanoparticles was analyzed in terms of particle number concentrations (PNC), size distributions and source strengths. The emission of nanoparticulate aerosols

reached peak PNC for particles in the range from 5 nm to 1 μ m with source strengths about 108 #/h in a background-filled environment and 1010 #/h in a practically particle-free atmosphere. No agglomeration was noticed for the released nanoparticles, suggesting that PNC was low enough to prevent coagulation and that particle diameters were over 80 nm. Results indicate that emitted matter was within the range of the most penetrating particle sizes and with source strengths similar to accidental scenarios.

Poster Presentation Session

Systems for capturing and recycling airborne engineered nanoparticles from occupational environments

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Abstract: The atmosphere is teeming in airborne nanomaterials with different particle size distributions. This situation is especially significant in occupational environments in which nanoparticles are being handled, both during synthesis and characterization as well as during their application. Usually, the elimination of airborne matter is carried out by filtration with adequate fiber screens, which control and reduce human exposure to nanoparticles.

On the other hand, the synthesis of specific engineered nanoparticles requires in most cases an outstanding effort in terms of material resources and research. Therefore, the presence of these engineered nanomaterials in breathable atmospheres supposes a potential risk for human and environmental health but also an economic impact for industries and consumers.

Here we report on a compact and convenient system to eliminate the hazards and recycle engineered nanoparticle aerosols. This design consists in a water-based jet mixer with recirculating water stream that captures airborne nanomaterials. Several nozzle arrangements and designs have been tested together with variable airstreams and water flows for achieving nanoparticle capture levels up to 90%.

Poster Presentation Session

Recent Developments in Risk Assessment Efforts for Nanosilver and Nanotitania

*Michael Tsang (University of Bordeaux, ISM, CyVi)**

Danail Hristozov (Ca'Foscari University of Venice)

Chengfang Pang (Ca'Foscari University of Venice)

Abstract: This poster will highlight the recent work in the area of human health risk assessment for engineered nanomaterials. This risk assessment will demonstrate the approach and software being newly created as a product of the Sustainable Nanotechnologies project, a large multi-national EU project as a part of the EU FP7 research programme. Exposure assessments for Nanosilver and Nanotitania will be conducted specifically for occupational and consumer scenarios, while exposure doses will be quantified using the NanoSafer model which is currently being updated in the SUN project. Dose-response data from the literature on these materials will be used to derive the benchmark dose lower bound and/or benchmark concentration as the point of departure. This poster will discuss the benefits, caveats and drawbacks from using the BMD approach for both nanomaterials, particularly in comparison with using NOAEL/LOAELs. Comparisons will be made to previous risk assessments made for these materials such as the US EPA's 2011 nanosilver risk assessment.

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Poster Presentation Session

Development Of A Nano Exposure And Contextual Information Database (NECID)

*Wouter Fransman (TNO)**

Johannes Pelzer (TNO)

Wiho Stöppelmann (TNO)

Abstract: For future research in studying exposure to nanoparticles, there is a need for an occupational exposure database. Amongst a working group of PEROSH institutes, IFA and TNO have developed a database structure called NECID (Nano Exposure and Contextual Information Database), which will include exposure data and contextual information. The database will facilitate the future comparing and sharing of nano exposure data, because the exposure data of different institutes are collected and stored in a harmonized way. The database is based on the characteristics of existing databases (ART database, MEGA) and the NANOSH dataset. As nanomaterials have distinctive characteristics and the measurement strategy is based on a multimetric approach, additional variables have been introduced. The proposed structure of the database covers a set of contextual core information variables in the database. Terms of use were composed for institutes and user-specific rights have been awarded for the entering, reading, reporting and export of data for different users. A first version of NECID has been released and is available to PEROSH partners and several external partners. A “calculation tool” is currently in development that will facilitate the statistical analysis and comparison of entered data and the reporting of the results from NECID.

Poster Presentation Session

Flow of Nanomaterials in Constructon and Demolition Waste in Switzerland

*Ingrid Hincapié (EMPA)**

Alejandro Caballero-Guzman (EMPA)^p*

Bernd Nowack (EMPA)

Abstract: Nanomaterials (NMs) used in the construction industry will enter recycling and construction waste through renovation and demolition of buildings. Information about NM flows in these processes is insufficient, thus the potential release of NMs into the environment and the implications of this release are unknown. We surveyed representatives from the Swiss construction industry to obtain information about NM applications and the amounts used in construction industry. The survey showed that NMs are mainly used in paints and cement. The most used NMs in construction are nano-TiO₂, nano-SiO₂, nano-ZnO and nano-Ag. We complemented this information with literature data and market reports found for paints. Then we estimated the flows of NM contained in paints to recycling and landfills with a semi-quantitative bottom up approach. The waste from paint is contained in materials like concrete, bricks or wood and the NMs' flows are determined by the flows of these building materials. The main amounts of NMs contained in paints will enter the recycling system (23 ton/y), followed by direct input into landfills (7 ton/y) and incineration (0.01 ton/y). Thus, we determined qualitatively NMs' potential release in the technical or environmental compartments. The potential for release of NMs is clearly high during recycling.

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Poster Presentation Session

Use of a Nanoparticles Size-Ladder Standard in Asymmetric Flow Field-Flow Fractionation Coupled to ICPMS

*Francisco Barahona (EC Joint Research Centre)**

Otmar Geiss (EC Joint Research Centre)

Josefa Barrero-Moreno (EC Joint Research Centre)

Abstract: The detection and characterization of nanoparticles (NPs) in aqueous matrixes is often addressed by asymmetric flow field-flow fractionation (AF4), traditionally in combination with different detectors, such as dynamic light scattering (DLS), multi-angle light scattering (MALS) and inductively coupled plasma mass spectrometry (ICPMS). Each type of detector is suited to provide complementary information and shows advantageous features as well as specific limitations/drawbacks. In this regard, the AF4-ICPMS on-line coupling is a powerful technique that allows the characterization of NPs in terms of size and mass concentration simultaneously. Although according to AF4 theory, information about the particle size can be obtained from the calibration with size standards regardless the nature of the particles, in practice the interactions between NPs and the permeation membrane within the separation channel often lead to miscalculated particle dimensions. In the same manner, losses of material in AF4 separation make quantification often difficult and recovery issues must be addressed under case-by-case (and size-by-size) bases. The use of pre-channel calibration with well characterised suspensions of multimodal NPs size standards of similar nature to the sample NPs (size-ladder) can overcome such issues in a pragmatic manner.

Poster Presentation Session

Extraction, Characterization and Determination of Fullerenes Nanoparticles in Aqueous Environments

*Justin Chun-Te Lin (Feng Chia University, Taiwan)**

Ronald Ling (Peking University, China)

Jesse Jen-Chung Luo (Peking University, China)

Abstract: Engineered carbon nanoparticles (NPs), such as fullerenes and carbon nanotubes, recently are detected in various aqueous environments by several researchers. However, numerous environmental factors and analytical procedures affect determinations of these trace and tiny materials. Three fullerenes nanoparticles (nC60, nC70 and nPC60BM) prepared by a sonication method are used to spike into tap water and reservoir water in order to analyze the environmental matrix effects. The three NPs are then characterized by a Nanoparticle Tracking Analyzer (NTA) for throughout profiling their size and size distributions. A new evaporation-redissolved method is proposed in this study to determine the actual concentrations of the as-prepared NPs in the aqueous phase since previous methods (e.g. evaporation or weighting) cannot give a practical and efficient quantitative basis. Liquid-liquid microextraction (LLME) is used to convert the spiked fullerene NPs from aqueous phase to organic phase (toluene) and determined by a UV-vis spectrometer. Recoveries of the extraction and characteristics of the three NPs were compared and evaluated the feasibility in the analysis in the real aqueous environmental samples.

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Poster Presentation Session

Stability of P25 TiO₂ and NanocylTM NC7000 Multi-walled carbon nanotubes in artificial freshwater for ecotoxicity using LUMiSizer 651: preliminary results

Andrea Brunelli (University Ca' Foscari of Venice)

Antonio Marcomini (University Ca' Foscari of Venice)

Abstract: The exponential growth of nano-based commercial products on the market have raised concern about the potential consequences for the environment and human health to the exposure of engineered nanomaterials (ENMs). Given the extensive uses and applications of nano-products, the aquatic environment is one of the main storage compartment. Therefore, the study of the behavior of ENMs in aqueous dispersions is of considerable importance.

In the present work, the characterization of the stability of two different ENMs, with regards to chemical composition, shape and size, i.e. the inorganic Aerioxide® P25 TiO₂ and the organic NanocylTM NC7000 Multi-Walled Carbon Nanotubes (MWCNTs), the latter provided in the EU-FP7 SUN project, dispersed at concentrations and medium relevant for ecotoxicology studies, was investigated by Multi-wavelength Dispersion Analyzer LUMiSizer® 651 (L.U.M. GmbH, Berlin). Exploiting Lambert-Beer and Stokes' Laws, the average particle sedimentation velocity as well as the particle size distribution (PSD) were investigated according to ISO 13318-2:2007, along all the sample length. We therefore propose the LUMiSizer® 651 as a robust alternative to other classic techniques to investigate the stability of ENM dispersions for fate and transport modeling.

Poster Presentation Session

Fate and Transport of Zinc Oxide Nanoparticles in Various Aqueous Environment Conditions

*Myunghye Lim (Korea Institute of Toxicology)**

Seong Min Hong (Korea Institute of Toxicology)

Yu Sik Hwang (Korea Institute of Toxicology)

Abstract: With ZnO NPs increasingly being manufactured and used for widespread applications, ZnO NPs will be released into natural and engineered aquatic systems during production, transport and use. The physical and chemical properties of ZnO NPs are easily changed by environmental factors. Therefore, the fate and transport studies of ZnO NPs under the different environmental conditions need to be studied. This work investigated on the dissolution of ZnO NPs in the presence of phosphate. The effect of humic acid (HA) and co-presence of phosphate on the dissolution of ZnO NPs was also investigated. Based on the results, the presence of phosphate and humic acid has a significant impact on the dissolution of ZnO NPs in aqueous solutions. In addition, the dissolution and sedimentation behaviors of ZnO NPs were studied in natural water samples. The presence of natural colloids significantly affects the dissolution and sedimentation of ZnO NPs. These results can provide a better understanding of fate, transport and toxicity of nanoparticles in natural water system.

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Poster Presentation Session

Solar-induced TiO₂-mediated photocatalytic inactivation of target microorganisms

*Theodora Velegraki (Aristotle University)**

Ioannis Poullos (Aristotle University)

Abstract: The present work investigates the experimental conditions and reaction kinetics of the solar-induced TiO₂-mediated photocatalytic inactivation of target microorganisms i.e. *Pseudomonas aeruginosa* and *Klebsiella pneumoniae*. The influence of varying parameters such as amount of photocatalyst, irradiation time, substrate concentration and matrix complexity have been thoroughly studied. High inactivation rates are achieved for both strains upon irradiation with simulated sunlight in the presence of 0.5 g/L TiO₂ (Degussa P-25). *K. pneumoniae* proves more resistant to the oxidative stress produced by photocatalysis than *P. aeruginosa*. At varying TiO₂ loadings (i.e. 0.25, 0.5 and 1 g/L TiO₂) the generated reactive oxygen species (ROS) result in complete bacterial inactivation; however, this is obtained at different amounts of accumulated energy i.e. *P. aeruginosa* inactivation requires accumulated energy equal to 1.6 – 2.5 kJ/L (i.e. corresponds to illumination time ranging between 30 min to 120 min), whereas *K. pneumoniae* for similar catalyst loadings requires higher amounts of energy i.e. 3-3.5 kJ/L (i.e. corresponds to real illumination time ranging between 90 min to 120 min) for complete inactivation. The nature of the aqueous matrix has an adverse effect on inactivation rate; the inactivation efficiency of both strains in real wastewater is strongly suppressed compared to the respective values for tap water and deionized water.

Poster Presentation Session

Environmental, health and safety impacts of the use of nanomaterials in the textile finishing industry. ECOTEXNANO LIFE+ project

*Socorro Vázquez (LEITAT Technological Center)**

Raquel Villalba (LEITAT Technological Center)

Natalia Fuentes (LEITAT Technological Center)

Jordi Mota (LEITAT Technological Center)

Marta Escamilla (LEITAT Technological Center)

Margarita Santamaría (LEITAT Technological Center)

Abstract: The use of nanomaterials is gradually increasing due to new properties addressed by nanotechnology based EU textile products. Such rapid proliferation results in a key environmental problem due to the lack of knowledge of their health and environmental impacts and subsequent effects on the ecosystem.

Within this scope, ECOTEXNANO aims to improve the environmental performance of best innovative solutions that incorporate nanoparticles in textile finishing industry. ECOTEXNANO addresses four functionalities: soil-release, UV-protection, antimicrobial and flame-retardant; selecting the most representative nanomaterials used in textile finishing processes by functionality. Environmental, health and safety impacts are being assessed by LCA of the manufacturing operations and Risk Assessment of the selected nanomaterials.

Demonstration is being developed into two pilot scale trials (Spain and Italy) to provide evidence of best practice in the application of nano-based techniques comparing with the conventional finishing chemicals. The results will provide the textile finishing industry a tool to support the risk assessment of nanomaterials along their life cycle and to bridge knowledge gaps on nanomaterials properties, hazard and exposure. It will launch further development of a network platform for stakeholders. Human health and environmental EU policy (REACH, CLP, biocidals, BREF for textile sector) will be analyzed for potential updating.

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Poster Presentation Session

Radioactive Labeling by Irradiation with Fast Protons for Study of TiO₂ NPs Biokinetics

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Abstract: Titanium dioxide nanoparticles (NPs) are an example of widely used NPs. These NPs find an application in different areas from white dye production to cosmetic industry. Due to their properties to absorb and scatter UV-radiation, they are used in sunscreens. NPs are more effective than macroparticles of the same compound, but in the same time they occur to be more toxic because of their direct influence on cells, therefore the problem of environment and health safety concerned to NPs use is extremely important today. TiO₂ NPs aren't an exception, due to their phototoxicity they are at the first lines of the hazardous inorganic NPs list and the problem of TiO₂ NPs safety is of the high actuality.

One of the nanosafety branches is in study of biokinetics of NPs in living organisms. The application of nuclear-physical methods is a possible approach for this purpose. Radioactive Labeling technique allows alerted tracing of inorganic NPs in complex biological tissues.

Thereby the aim of the present work was in labeling of TiO₂ NPs. The difficulty of this problem was in choosing of ionizing irradiation type, producing isotopes of Ti with quite long half-life and satisfactory cross section. Theoretical analysis of this question led to conclusion that irradiation only with fast protons and alpha-particles provide necessary isotope characteristics of Ti and it has been proven experimentally. The work was financially supported by Ministry of Education and Science of the Russian Federation (grant № RFMEFI57514X0072).

Poster Presentation Session

The JRC Repository of Nanomaterials: providing representative test materials for methods validation in nanoEHS research and regulation

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Abstract: The Joint Research Centre of the European Commission (Ispra site, Italy) hosts a repository of representative (1) nanomaterials (NMs). These NMs are studied in the OECD WPMN testing programme and distributed to various European organisations, and beyond, in the frame of large collaborative research projects, such as EU-funded projects (MARINA, ENPRA, NANOGENOTOX, NANoREG, NanoMile, QualityNano, etc.). Several thousand vials have been distributed for free worldwide. Sets of vials of a given NM contain subsamples that originate from the same batch. This is of key importance for promoting better reproducibility and reliability in harmonisation and validation of testing methods and for comparability of results using different protocols. JRC's collection constitutes the first set of NMs that have been extensively characterised (2) for physical-chemical properties and thoroughly tested for (eco)toxicological and reactivity hazards. They can therefore be used as benchmarks for future research and regulatory development, and for supporting the development of regulatory-relevant testing methods. Accordingly, the JRC Repository has great potential as supporting tool for global harmonisation in nanoEHS testing and assessment.

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Poster Presentation Session

A Risk Ranking Approach for Nano-Enabled Applications for the US Army

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Abstract: In recent years, there has been an increase in the use of decision support tools for engineered nanomaterials (ENMs) given the challenges of applying traditional risk assessment. Risk ranking tools are one type of decision support tool that can rank ENMs or nano-enabled products in order to identify the highest (or lowest) ranked materials and/or products. Working with the United States Army Center for Environmental Health Research, we developed a risk ranking tool termed “Tool for ENM Application Pair Risk Ranking” that uses a ranking algorithm that incorporates both the physicochemical characteristics of the ENMs as well as the characteristics of the Army equipment, focusing primarily on Army worker and soldier health. This ranking tool is unique since real-world ENM applications and equipment containing ENM used in research or full-scale field applications were considered to perform the relative risk ranking rather than primarily e.g. hypothetical or pristine ENMs. Among other results, we found that inhalation from accidental exposures to carbon nanotubes and copper flakes incorporated into energy and obscurant materiel by Army workers rank highest relative to the other items evaluated in this baseline assessment.

Poster Presentation Session

Toward Achieving Harmonization in a Nano-cytotoxicity Assay Measurement through an Interlaboratory Comparison Study

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Abstract: Design and development of reliable cell-based nanotoxicology assays are important for evaluation of potentially hazardous engineered nanomaterials. Challenges to producing a reliable assay protocol include working with nanoparticle dispersions and living cell lines, and the potential for nano-related interference effects. We demonstrate the use of a 96-well plate design for a nano-cytotoxicity MTS cell viability assay. A detailed protocol and an inter-laboratory comparison are used to illustrate the variability of the assay with NH₂-polystyrene nanoparticles. Data on both the within and between laboratory system controls can be used to evaluate the largest sources of variability in the protocol. This study suggests that a high level of agreement between each of the laboratories can be achieved, but consideration of protocol details such as cell line ID, cell rinsing, media removal, and nanoparticle.

Poster Presentation Session

Quantitative testing of nanoparticle release in the lifecycle of coatings – example spray application

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Abstract: The coating industry processes numerous materials within their products, which are covered by the definition of nanomaterials according to ISO/TS 80004-1:2010. There are several potential release scenarios for nano-objects studied during processing and use of coating products in a national German project, covering powder, suspension and composite state.

In order to characterize particulate emissions during spray-can and spray-gun application, a simple spray channel was developed. To ensure occupational and instrumental safety, the spray channel was implemented in a special designed experimental setup. The spray-aerosol characterisation was performed according to the systematic approach, i.e. among others macroscopic spray process characteristics were analysed in addition to the particulate release. An Engine Exhaust Particle Sizer, an Aerodynamic Particle Sizer and a Condensation

Particle Counter were operated for the determination of number-weighted particle size distributions and particle number concentrations from a few nanometres up to several micrometres. Particle nature analyses were performed on electrostatically precipitated spray aerosol particles by means of scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray spectroscopy. Release data will be given for four types of coatings doped with three types of nanoparticle additives that were aerosolized by two kinds of spray cans a manual gravity spray gun.

Poster Presentation Session

Lignin as a new sustainable precursor for carbon fibre

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Abstract:

Lignin is an alternative precursor that is a sustainable resource material, the cost of which is largely independent of oil prices when compared to state-of-the-art known precursors (e.g. PAN). It is a complex chemical compound commonly derived from wood via Kraft pulping. Lignin will become increasingly available as a by-product from cellulosic ethanol production as bio-refineries are built.

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As a potential petroleum feedstock replacement, lignin can reduce environmental impacts such as carbon emission. Due to its complex chemical structure, lignin is currently underutilized. Exploiting lignin as a precursor for carbon fibre adds high economic value to lignin and encourages further development in lignin extraction technology.

Lignin has heterogeneous structure and lack of a well-defined chemical structure, being rather demanding as carbon fibre precursor. Lignin is a high molecular weight aromatic polymer with three dimensional structure. The chemical structure of lignin monomers and linkages that constitute these networks differ depending on morphological regions of the wood cell walls (middle lamella vs. secondary wall), different types of cells (vessels vs. fibres) and different types of wood (softwood vs. hardwood). For native lignin, no method could isolate it from plants so far. Chemical and physical modifications are necessarily for lignin isolation. The chemical processing of lignin isolation includes alkaline, acidic, or organic solvent processing, and lignin often undergoes fragmentation and degradation during chemical processing. The molecular weight, functional groups, degree of condensation, types of inter-monomeric linkages, and types and ratios of monomeric units vary depend on the type and length of chemical processing. Therefore, the degree of polymerization of native lignin is quite difficult to measure.

The manufacture of carbon fibres from lignin precursors involves isolation, melt spinning, stabilisation, carbonisation and graphitization. A crucial step in the process of manufacturing carbon fibres from lignin is the spinning of the fibres. The following methods can be employed; wet spinning, dry spinning, melt spinning. Melt spinning is used mostly for thermoplastic materials, since it involves the melting of polymer granules. It is used to manufacture pitch based carbon. It cannot be used for PAN based fibres, which require wet or dry spinning. Lignins are mostly used with melt spinning. Not all lignins are eligible for this process however, since they must exhibit thermoplastic properties (e.g. detectable glass transition temperature).

Very few (if not none) of the carbon fibres from lignin have attained the mechanical properties of the general performance (GP) carbon fibre from pitch. One of the most active research groups studying carbon fibres has set a target to manufacture a lignin-based carbon fibre with a tensile strength of 1.72 GPa and a modulus of 170 GPa as sufficient mechanical properties for the automotive industry. The best reported carbon fibre thus far originates from hardwood Alcell lignin purified using an organic solvent and exhibits a tensile strength of 1.1 GPa and a modulus of 69-83 GPa.

Acknowledgments

The support from the EU FP7 Project "Functionalized Innovative Carbon Fibres Developed from Novel Precursors with Cost Efficiency and Tailored Properties" (FIBRALSPEC) under Grant Agreement no. 604248 is greatly acknowledged.

Poster Presentation Session

Pulmonary effects of nano Copper oxide in a Short-term inhalation study (STIS)

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Abstract: The inhalation route is of special concern for worker and consumer safety. Short-term inhalation testing has recently been proposed as a cost-effective test to generate a valuable data set for risk assessment (Ma-Hock et al., 2014). This includes apart from the generally required pathology, biochemistry and tissue burdens.

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Here we tested nano-sized copper oxide (nano CuO), a wood protection/anti-microbial agent, in a short-term inhalation protocol (STIS). Rats were exposed by nose-only to a 6-hour equivalent concentration of 0, 0.6, 2.4, 3.3, 6.3 and 13.2 mg/m³ CuO, with a primary particle size of 15-20 nm and a MMAD of 1.5 μ m (σ 0.38). Following a 5-day exposure period, lung burdens were assessed and toxicological examinations were performed the day after the last exposure and after a recovery period of 3 weeks.

A dose-dependent lung inflammation and cytotoxicity was observed that followed the lung burden at day 6. These adverse effects were absent after the recovery period. Histopathological examinations indicated alveolitis, bronchiolitis, vacuolation of respiratory epithelium and emphysema in the lung starting at 2.4 mg/m³. In the recovery groups, inflammation remnants were still observed at the highest dose groups. Degeneration of the olfactory epithelium in the nose was observed starting at 6.3 mg/m³ and fully recovered. No histopathological changes were detected in brain, olfactory bulb, spleen, kidney and liver. The STIS protocol proved to be a useful tool to assess the hazard of nano CuO and information can support grouping and categorization of (nano)materials for risk assessment.

Nanotechnology : the missing piece of the life puzzle

Gilbert M. Rios (European Membrane House (EMH))

Abstract: In all the countries the appetite of scientists for nanotechnology, and the belief in its ability to provide more efficient solutions to technical issues that are facing our societies, have been growing very fast during the last decade. Also, a tremendous development of membrane technologies has led to consider them like "dominant technologies", with the emergence of a new think-tank / action-tank named "membrane engineering" and a lot of applications with environmental issues (water, air...). Because many of these technologies depend on nano-scale processes, it is reasonable to expect a strong impact of nanotech on performance of membrane systems of the future, particularly in tremendous field such as desalination. Nature on its side has solved long ago the problem of controlling the selective transfer of water and salts, with wonderful nano-tools: aquaporins, ion conducting channels ... Today researchers are trying to imitate nature with new aquaporin-laced polymer membranes, aquaporin mimicking carbon nanotubes... In what extend human achievements for highly efficient membranes have been delayed by our ignorance of nanotech? In what extend sustainability may be affected by revolutions in progress on this area? This is the kind of questions that our presentation intends to deal with.

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